

**SCIENCE REQUIREMENTS DOCUMENT**

**PHYSICS OF COLLOIDS IN SPACE II**

**PCS-II**

**Version.3.2**

**September 18, 2000**

Prof. David A. Weitz  
Principal Investigator  
Div. of Engineering and Applied Sciences / Department of Physics, Harvard University  
Cambridge, MA 02138  
Tel: (617) 496-2842  
e-mail: weitz@deas.harvard.edu

Prof. Peter N. Pusey  
Co-Investigator  
Department of Physics, The University of Edinburgh  
James Clerk Maxwell Building, King's Buildings, Mayfield Road  
Edinburgh, EH9 3JZ UK  
Tel: (44) 131-650-5272  
Fax: (44) 131-662-5902  
e-mail: pusey@mail.ph.ed.ac.uk

Dr. Urs Gasser  
Post-doctoral Fellow  
Div. of Engineering and Applied Sciences / Department of Physics, Harvard University  
Engineering Sciences Laboratory, Room: ESL 201  
40 Oxford Street  
Cambridge, MA 02138  
Tel: (617)496-7451, fax: (617)496-3088  
email: gasser@deas.harvard.edu

Dr. Subramanian Sankaran  
Project Scientist  
National Center for Microgravity Research  
NASA Glenn Research Center at Lewis Field,  
21000 Brookpark Rd., M/S 110-3,  
Cleveland OH 44135-3191  
Tel: (216) 433-9335  
email: Sankaran@grc.nasa.gov

Science Requirements Document (SRD)  
**PHYSICS OF COLLOIDS IN SPACE II**  
(PCS-II)

David A. Weitz

Principal Investigator  
**Harvard University**

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

Peter N. Pusey

Co-Investigator  
**Univ. of Edinburgh**

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

Urs Gasser

Post-doctoral fellow  
**Harvard University**

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

**CONCURRENCES:**

NASA - Glenn Research Center

Michael P. Doherty

Project Manager

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

Subramanian Sankaran

Project Scientist

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

NASA - Headquarters

Bradley M. Carpenter

Lead Experiment Scientist

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

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# 1 Executive Summary

## 1.1 Description of Experiment

The goal of this experiment is twofold: to carry out further investigation of critical, fundamental problems in colloid science, and to fully develop the evolving field of “colloid engineering,” to create materials with novel properties using colloidal particles as the precursors. In both cases, gravity-driven sedimentation and convection precludes these experiments from being carried out on earth, and requires a microgravity environment to address many of the most critical questions.

This experiment is envisioned as a direct follow-on to the Physics of Colloids in Space I (PCS-I), which is currently scheduled to fly for about 12 months in the International Space Station between 2000 and 2001. We emphasize, therefore, that since the most crucial predecessor experiment has not been carried out, the experiments proposed here must, of necessity, make some assumptions about the outcome of PCS-I. However, since the preparation time scales for these experiments are so long, this is a necessity. Therefore, we must make reasonable assumptions about the outcome of PCS-I, and incorporate these into the design of PCS-II. However, because of the long lead time required, and the likelihood of new results becoming available before the flight, due both to PCS-I and to our continuing ground-based research, we have designed the experiments proposed here to be relatively flexible, in that it will be possible to modify their details in a straightforward fashion, to accommodate any changes dictated by unexpected results from PCS-I, and developments in ground-based research which occur before PCS-II. Our goal is to ensure that the very best experiments are flown, and that the very best value is received for the investment in these experiments. As we note below, this places specific requirements on the design of the hardware.

This experiment will focus on two classes of colloidal samples. The first is binary alloys. These contain a mixture of two different colloidal particles. If their size ratio,  $r$ , and volume fraction,  $\phi$ , are adjusted appropriately, the particles will self-assemble into ordered binary alloy crystal structures. In PCS-II, we will use colloidal particles of different materials to make binary alloy crystals, significantly extending our applications of colloid engineering. The second set of samples will be a mixture of colloidal particles with polymers. The addition of the polymers induces a controllable attractive force, due to depletion, between the colloidal particles. This attractive force facilitates the formation of other structures. In addition, the presence of an attractive force induces new phase behavior in the colloidal suspensions.

To allow all the properties of the materials to be measured, and to allow a degree of proactive control over the structures and properties of the materials produced, we propose to base the experimental apparatus on an optical microscope. This will allow unprecedented flexibility and control, essential to fully accomplish the goals of this work. The microscope will be equipped to allow direct visualization of the particles in real space, using both bright field and differential interference contrast (DIC) imaging, as well as fluorescent imaging; in addition, it will allow both dynamic and static light scattering

from the samples to determine Fourier space information. The microscope will also be equipped with laser tweezers to manipulate the structures formed to achieve specific effects. In addition, there will be confocal microscopy to allow strongly scattering samples to be studied and to provide 3D real-space information. Finally, because of the very small sample volumes required, the apparatus will be able to contain between 500 and 1000 samples in a very compact form, allowing the requisite sample variation to be achieved.

An important feature of this experiment is that it will be flown simultaneously with the second version of the PH<sup>A</sup>SE experiment, conducted by Paul Chaikin and Bill Russel of Princeton University. This experiment requires an apparatus of very similar design to that of PCS-II; as a result, the equipment is specified in a fashion that optimizes the requirements of both experiments. This is a highly cost effective method of conducting two distinct experiments, taking full advantage of a single apparatus.

## **1.2 Scientific Knowledge to be Gained**

These experiments will provide a unique example of the use of colloid engineering to synthesize new materials with novel properties. The goal is to exploit the long range ordered structures formed using the self-assembly of colloidal particles. The use of mixtures of two different materials greatly increases the flexibility of the resultant structures; for example, the characteristic length scale of the structure can be set by one material, which could be an inert plastic, while the second material could have some completely different property, and could, for example, be an optically active semiconductor particle. This provides an opportunity to synthesize structures that are ordered on the length scale of light in all three dimensions, and such materials should have fascinating new properties. For example, they may be suitable for optical switches or filters, or as photonic band gap materials. Fabrication of 3D ordered structures with traditional lithographic methods is very difficult, and has not been done on the optical length scale; the use of colloidal materials allows the structures to be self-assembled, providing a new method for materials synthesis. In addition, we will study the phase behavior and crystallization properties of these binary alloys. This will provide additional insight into their growth allowing us to further tailor the crystal structure.

We will also study the properties of mixtures of colloids and polymers where the addition of the polymer induces weak attractive interactions between the colloidal particles by the depletion mechanism, leading to a rich phase behavior for the colloidal particles. We will focus on the behavior near coexistence regions, where two or three phases exist simultaneously in the sample. We will study the structure and behavior of these phases, addressing critical questions that have been obscured in previous studies because of limitations imposed by sedimentation. For example, we will study the nature of the fluid droplets that form and will attempt to measure their interfacial tension by measuring their shape fluctuations. We will study the crystallization of the solid phase, measuring both the structure and the morphology of the crystallites. We will investigate whether the crystals are formed initially in the fluid droplets or whether they can sublime from the gas phase. We will also investigate the potential of using this weak attractive

interaction as an alternate means for controlling the growth of colloidal crystals for use as new materials.

### **1.3 Value of Knowledge to Scientific Field**

Although there has been considerable interest in the use of self-assembly for new routes of materials synthesis, relatively little has been done with colloidal particles as precursors. The use of binary alloys is a promising method to obtain additional flexibility in the design of new materials; however it has not been extensively explored. One of the main impediments in its use is the problem of differential sedimentation of the colloidal particles if the two types have different densities; this restricts most studies to particles of the same material, but of different sizes. These studies will be the first to explore this exciting and promising form of colloid engineering, by using particles that have both different sizes and are made of different materials.

The study of weakly attractive interactions between colloidal particles has mainly focused on their phase behavior. However, this work has generally been restricted to measuring the relative quantities of the different phases that are formed; thus we have not taken full advantage of the colloidal scale of the particles, which should allow much more information to be learned about the nature of the formation of these phases. Much of the impediment for this has been the gravity-induced sedimentation. While this is essential for determining the relative quantities of each phase formed, and hence the phase diagram, it also obscures any study of the structures of the different phases. Thus these experiments offer the first opportunity to measure the behavior of these systems. In addition, this will be the first time that an attractive interaction has been used in the formation of new materials with colloidal particles as precursors.

### **1.4 Justification of the Need for Space Environment**

The formation of colloidal crystals is strongly affected by sedimentation; this is most graphically demonstrated by the results of the experiments of Chaikin and Russel, who showed that the morphology of colloidal crystals grown in space is completely different from that grown on earth. The primary reason for this is sedimentation. As the crystals sediment, the shear of the fluid flowing past their edges is sufficient to destroy them. In addition, the sedimentation time of the crystals rapidly begins to compete with the diffusion time of the accreting particles, significantly changing the growth mechanism. While some of this effect can be mitigated by buoyancy matching, this is not completely effective, even at the best level of buoyancy match that can be achieved. By contrast, performing the experiments in microgravity significantly reduces the sedimentation, and eliminates the problems. Thus very large crystals can only be grown in microgravity. This is essential both to study the very delicate structures of the colloid-polymer mixtures, and to allow the binary alloy colloidal crystals to grow. In addition, when colloidal particles of different materials are used, it is even more essential to perform the experiments in microgravity; otherwise the differential sedimentation of the different particles will prevent growth of any crystals.

## 2 Background

### 2.1 Description of Scientific Field

Colloidal suspensions exhibit a rich and varied range of properties. They are of great scientific interest, as well as of great practical importance. They can be synthesized with exquisite precision and control, and can be formed from a wide range of materials. Colloidal particles can be made highly monodisperse in size. The interactions between the particles can also be finely tuned, and can vary from highly repulsive, to weakly attractive, to strongly attractive. The particles can be induced to self-assemble into a wide range of structures; many of these have long-range order. They can serve model systems for the study of fluid and solid properties, with the colloidal particles playing the role of atoms or molecules. The relaxation times that characterize their behavior are much longer than those of atomic or molecular materials, making them much more accessible to experimental probes. In addition, the larger size of the colloidal particles facilitates the study of the structure and dynamics of the suspensions, allowing, for example, the use of optical techniques such as static and dynamic light scattering and laser crystallography, or Bragg scattering.

Under appropriate conditions, monodisperse colloidal particles can self-assemble into crystalline structures with long range periodic order [1], driven solely by entropy. If particles of different diameters are mixed together, these same entropic effects can lead to the self-assembly of binary alloy crystals [2,3]. Several different crystalline structures have been observed, and more are predicted to occur [2-5]. Experimental studies to date on binary alloy crystals have been restricted to the use of particles of the same material, facilitating their study. The samples can be conveniently index matched to the surrounding fluid, reducing van der Waals interactions between the particles and eliminating multiple scattering, allowing the structures to be studied with light scattering methods. However, because of the large potential phase space in mixing particles of different sizes, determined for example by the ratio of particle sizes,  $r$ , the individual particle volume fractions, and the total volume fraction of the suspension,  $\phi$ , knowledge of these potential structures is still incomplete. In addition, knowledge of the nucleation and growth, as well as the ultimate morphology of these crystals is still very limited.

The high degree of control over the synthesis of colloidal particles and our ability to finely tune the interaction between them also makes it possible to use colloidal particles as precursors for forming new materials; these should have unique and novel properties. This new route to materials synthesis has been dubbed “colloid engineering.” For this, the use of binary alloys can greatly extend the potential for making different materials and add considerable flexibility to the type of materials synthesized. In particular, self-assembly of crystalline binary alloy structures is not restricted to the use of colloidal particles of the same material. Instead, it should be feasible to mix particles of different materials provided they are stable against aggregation. This will allow the formation of materials with unique and fascinating properties. For example, these



colloidal alloys may form the precursors for very high quality ceramics. Alternatively, one set of particles could be plastic and the other set of particles could be a metal or a semiconductor. After formation of the binary superlattice, sintering at a temperature above the glass transition of the plastic could provide a plastic sheet containing the other particles in ordered arrays. Such a material should have unique optical, or even electronic, properties. For example, this may be a simple method for fabricating an array of quantum dots that has useful optoelectronic properties. Alternatively, colloid engineering may provide a simple route to the synthesis of photonic band gap materials [6,7], or structures that have a greatly reduced phase space available for radiation [8]. Current routes for fabricating photonic band gap materials in the optical regime rely on three-dimensional lithography, which is a very challenging and difficult process; colloid engineering may offer a simple method for making these materials that completely bypasses many of these difficulties. These superlattices could also be used as novel optical switches or displays; instead of using solid colloidal particles, monodisperse emulsion droplets or colloids filled with liquid crystal molecules could be used to form the structures, allowing their optical properties to be switched by application of an external electric field. The switching voltage is a function of the particles size, making it feasible to switch a Bragg scattering matrix on and off by switching the large droplets in a superlattice, making the smaller one Bragg scatter. This could form the basis for a novel optoelectronic display technology that not only switches light, but also controls the direction or color of the displayed light. Many other novel materials can be envisioned.

The self assembly that leads to the formation of binary alloy crystals relies primarily on entropy; the interparticle interaction is strongly repulsive at short range, and is essentially zero at longer range. As a result, the structures that form are controlled solely by free volume and particle packing considerations. Completely different behavior ensues if there is a weak attractive interaction between the particles. An effective attractive interaction can be induced between the colloidal particles through the addition of polymer to the solution, resulting in a depletion-induced attraction. This is still an entropic effect, and thus the effective energy scale is still the temperature,  $k_B T$ . This is a highly controllable attractive interaction; the range is set by the size of the polymer molecules and its strength is set by their concentration. The weak attraction between the particles leads to a wide range of interesting phase behavior, that has many features in common with traditional phase diagrams of coexisting gas, liquid and solid phases [9]. For example it is possible to find regions where there are two and even three phases in coexistence. It is also possible to induce a sufficiently large attraction that the phase separation is kinetically constrained by the formation of a gel-like structure [10,11]. The phase behavior of colloidal particles with an attractive interaction induced by depletion has been studied for several different systems, including emulsion droplets [11], charge-stabilized polystyrene spheres [12], and PMMA particles [11].

While the basic phase diagram is well understood, much less is known about the kinetics of the phase separation process and the formation of the distinct phases after the suspension has been homogeneously mixed. In addition, the possibility of a controllable attractive interaction between colloidal particles has significant consequences for colloid engineering, offering new, and heretofore unexplored opportunities for creating different colloidal structures.

## 2.2 Current Application for Research

The primary goal of PCS-I is to develop the basic principles for synthesizing several different sorts of materials, to determine the fundamental properties of the growth of these materials, and to begin the study of their basic properties. PCS-II will continue this program, building on the results of PCS-I. However, the primary goal will be to more fully develop colloid engineering, to synthesize new materials, and to more fully characterize their properties. The type of materials that will be studied in PCS-II will be broader than in PCS-I, allowing a more complete suite of materials to be synthesized. In addition, the nature of the experiments that will be performed will be significantly different. As a result, the equipment required differs from that required for PCS-I

In PCS-I, three classes of colloidal materials will be studied. These include ordered crystalline samples; mixtures of colloidal particles with other species, primarily polymers, which induce a weak attractive interaction allowing us to precisely tune the phase behavior of the mixtures; and highly disordered, but very tenuous structures which possess their own unique symmetries and their own unique properties. In PCS-II, we will emphasize materials synthesis in PCS-II, and will focus on only the first two of these classes of materials, and will not pursue further studies of the very interesting fractal colloidal aggregates.

### 2.2.1 Binary Alloy Crystals

In PCS-I, we will study the formation of binary colloid alloys made of a single material, poly-methylmethacrylate, or PMMA. This will allow us to index match the colloids to the surrounding fluid and to use the full slate of light scattering analysis tools available to the PCS-I apparatus. The goal of the PCS-I experiment will be to develop a better understanding of the fundamental crystallization mechanisms that control the crystal growth, and to explore the properties of the alloys.

In PCS-II, we will exploit the knowledge gained from PCS-I, as well as all the other flight and ground based experiments we have conducted. We will focus on making new binary alloy crystals comprised of colloidal particles of different materials. The goal will be to synthesize structures that have interesting optical properties. Many of these properties arise because the periodicity of their lattice constants of the crystals is on the same scale as the wavelength of light; this scale is set by the choice of particle size. Because their structure is periodic, binary alloy crystals diffract light. However, the diffraction is not limited to a single direction, as is, for example, a simple grating, but can instead potentially be in all three directions simultaneously. Because of the 3D structure, the fabrication of these diffraction gratings with traditional lithographic techniques is extremely difficult. By contrast, the self-assembly of colloidal particles may make it much simpler.

In PCS-II, we will likely still use PMMA particles as one of the colloids; they are well understood, and provide a useful space-setting material; they are optically inert, and can be synthesized in very monodisperse suspensions with finely controlled sizes. The second colloidal particles will probably be either metallic particles, which will be useful for the purpose of making optical filters, or semi-conductor particles, which will be

useful for making optically active materials. In addition, we may use tertiary mixtures wherein the smaller particles are composed of mixtures of PMMA particles and a small fraction of the optically active particles, to allow us to dope the binary structure with only a small fraction of the optically active material. We also plan to use other materials to achieve different properties for the final structures. We plan to use particles that contain a liquid crystal within them. The optical properties of the liquid crystal can be significantly modified by the application of an external electric field, allowing an additional degree of control over the properties.

While many studies of the PMMA binary alloys can be carried out in our ground based research program, relatively little work will be possible with most of these mixtures of different materials. The key problem is the difference in the densities between the two particles. This makes it intrinsically impossible to buoyancy match the particles, as only one of the species can be buoyancy matched. As a result, many of the initial measurements will have to be carried out in microgravity. Our earlier studies will have identified the optimal phase space for formation of binary alloy crystals from PMMA, in terms of the optimal particle size ratios and volume fractions for a given structure. However, because the particles will be of different materials, the interparticle interactions will most likely be slightly different, requiring a somewhat larger steric stabilization of the particles. This may result in a slight modification of the interactions, changing the phase behavior. As a result, we will need to deploy a wider range of samples in the microgravity experiments to allow us to extend the boundaries of the phase space explored.

### 2.2.2 Colloid-Polymer Mixtures

In PCS-I, we will explore the bulk properties of samples of attractive particles, using the scattering tools available in the apparatus. This will enable us to follow the dynamics of the phase separation after homogenization, and will probe the kinetics of the formation of the different phases. This will provide important macroscopic information about the nature of the phase transitions. However, this will leave many crucial questions unanswered. Since the sample size will be relatively large, the light beams will probe an extended region of the sample, inevitably measuring a mixture of phases, and precluding the investigation of any individual phase. In PCS-II, we will have the facilities to probe very small sample volumes and to measure the behavior of isolated regions within these samples, allowing us to measure the properties of only single phases.

Among the key issues we will address is exactly how the phase separation proceeds. For example, when three phases coexist, we will investigate the mechanism for the formation of crystals, to determine whether the system first separates into a gas and fluid with the fluid further separating into a liquid and solid. If this is the case, then the crystals are formed in the fluid phase. Alternatively, some solid may sublime directly from the gas phase, while the remainder comes from the fluid phase. We will also investigate the nature of the droplets of liquid as they form, and will determine the surface tension of these droplets by studying their fluctuations. The surface tension should be extremely small and such an effect has never been determined in ground based measurements because of the low magnitude. However it should be possible in PCS-II.

We will also investigate the nature of the crystals structures formed by the depletion attraction. When monodisperse particles crystallize through entropic hard sphere repulsive interactions, there is apparently very little energetic difference between two close packed structures, face centered cubic (FCC), and hexagonal close packed (HCP). As a result, the structure formed is a mixture between the two, a random stacking of hexagonal close packed planes (RCP) [13]. By contrast, the structure of attractive particles is still not well determined. However, it is quite conceivable that with an attractive interaction, one structure will be preferred over others. This would be very useful for colloid engineering; RCP structures are strictly speaking not true crystals at all, as they lack long range order in all directions. As a result, they exhibit Bragg rods rather than Bragg points in  $q$ -space, which would be deleterious to their use in any photonic structure. Thus we will explore whether it is possible to create more highly ordered structures by means of an attractive interaction.

### 2.3 Brief Account of Prior Research

It has long been known that monodisperse colloidal spheres suspended at high concentrations in a liquid can, in natural Brownian motion, crystallize, to form arrays with long-ranged order [1,14,15]. More recently, the crystallization behavior of binary mixtures of particles of two different sizes has been investigated [3,5,16,17]. Under certain conditions, it was found that “hard-sphere” particles (colloidal PMMA) at size ratio 0.58 formed both the  $AB_2$  and the  $AB_{13}$  superlattice structures.  $AB_2$  consists of a simple hexagonal arrangement of large A particles, with the smaller B particles filling all the interstices between the A layers.  $AB_{13}$  is a remarkably complex structure. Icosahedral clusters of 13 small B particles are body centered in a simple cubic lattice of A particles; the icosahedra are rotated by  $90^\circ$  between adjacent cubic subcells so that the unit cell of the structure consists of eight subcells containing 112 particles. These two structures were identified both by static light scattering (“powder light crystallography”) and by electron microscopy of the dried suspensions [16,17].

The phase behavior of colloidal particles with an attractive interaction induced by depletion has been studied for several different systems, including emulsion droplets [18], charge-stabilized polystyrene spheres [12], and PMMA particles [11]. As the strength of the attractive interaction is increased by increasing the polymer concentration, the fluid-solid coexistence extends over an increasing range of colloid concentrations. However, the approach to the ultimate equilibrium structure becomes obscured by the kinetics of the phase behavior. As the polymer concentration is increased, the strength of the attractive interaction becomes so large that the colloidal particles form a gel-like structure [10]. This is characterized by a fractal structure at short length scales and a liquid-like ordering at larger length scales, resulting in a ring of intense light scattering at low angles. Ultimately, this gel-like structure should anneal into a crystalline order; however, under normal gravity the gel can not support its own weight and ultimately collapses, leading to macroscopic phase separation, obscuring the true equilibrium behavior. When the potential is weaker, crystallization of the particles can be induced by the depletion. The structure and morphology of these crystals may differ significantly

from those formed at higher concentrations by purely repulsive interactions; however, this behavior is obscured by sedimentation and has not been studied.

The NASA-supported work of the two PI's began in June of 1994. Since then considerable progress has been made, both in ground based experiments, and in support flights performing glovebox experiments aboard the Russian space station MIR. These are small, relatively lower risk experiments. However, they are essential to the program, as they provide us direct experience with actually performing experiments in space; they also provide a critical test to determine the effects of microgravity on our samples. Thus, one of their main goals is to help mitigate the risk in the PCS-I experiment. Since we will have only eight sample cells in PCS-I, and since the experiment will have a duration of approximately 12 months, we must ensure that samples we choose are optimized. The glovebox experiments provide a much larger number of samples, at a much lower cost. Although these samples can not be studied in as great detail as the PCS-I samples, we can use the glovebox results to help define the optimum samples for future in depth study in PCS-I. Three glovebox experiments have been performed to date, with a fourth scheduled for later in the fall of 1998, this time aboard the shuttle during the John Glenn mission. We briefly review the progress of both the glovebox experiments and the ground-based work, and include a brief account of the work planned for PCS-I. Further information about the results obtained from the glovebox experiments is available in a series of reports that have been, or are currently being prepared.

### 2.3.1 Glovebox Experiments

Three glovebox experiments have flown to date. Two of the experiments were designed to take pictures of ten samples to determine whether or not crystals grew, and to take video images of other samples over a shorter period of time using a low magnification lens. These experiments were called BCAT-I and BCAT-II for Binary Colloid Alloy Test. They were designed primarily to test the phase behavior of different mixtures of binary colloid alloy samples to determine whether the optimum mixtures identified in ground-based research were also optimum in microgravity. This determination is essential for PCS-I, where only a very small number of samples are to be flown; it is thus essential to ensure that the optimum samples are chosen.

BCAT-I successfully produced binary alloy crystals of the  $AB_{13}$  structure. Samples were chosen near the optimal size ratio of  $r \approx 0.58$ , and at several different total volume fractions. Interestingly, the optimum volume fraction for the crystal growth turned out to be  $\phi \approx 0.54$ ; this was higher than the optimum value on earth. This highlights the difference between results obtained on earth and those obtained in microgravity; this result is also extremely useful in planning for PCS. The results of BCAT-I also included the first observation of the persistence of colloidal crystals formed from monodisperse emulsion particles. On earth, these emulsions cream and, even though crystals do form, they do not persist when the emulsion creams. These results suggest that this may be due to the creaming; as the crystallites increase in volume fraction, they become unstable to rearrangements. This may be due to the intrinsic instability expected for an FCC (or RCP) lattice of particles with liquid films at their interfaces; these films must then meet the Plateau criteria for stability which can not be

done for an FCC structure [19]. Finally, the video component of BCAT-I also proved conclusively that the instability of the kinetically arrested gel-like structure formed upon the addition of high concentrations of polymer to induce a very strong depletion attraction among the PMMA spheres is gravity-induced. All earth experiments have shown that this gel structure collapses after some delay time, which depends on the strength of the attraction. Such a collapse precludes investigation of the long term stable state of the sample, which is completely unknown. The collapse was not observed in microgravity, but there was insufficient time to monitor the evolution of the long term structure.

BCAT-II tested a different series of binary alloy mixtures. A goal here was to further explore the phase boundaries of the region where good colloidal crystals form as  $r$  is varied. The samples chosen for BCAT-II had  $r \approx 0.61$ , which is slightly to the high side of the optimum value determined on earth. The goal was to investigate whether the optimum value of  $r$  changes as does that of  $\phi$ . The results suggested that this size ratio is very inefficient in forming colloidal crystals, implying that the optimum value of  $r$  is the same in microgravity as on earth, unlike the value for  $\phi$ .

The third experiment, which was chronologically the second one, was called CGel for Colloidal Gel. This experiment was supposed to reuse the apparatus flown by Chaikin and Russel, in their glovebox experiment, CDOT (Colloidal Disorder-Order Transition). This apparatus allows for rudimentary static and dynamic light scattering to be performed. CGel was designed to perform light scattering studies of all three classes of samples to be flown on PCS-I, including the binary alloys, the colloid-polymer mixtures and the fractal colloidal aggregate gels. A special in-situ mixing apparatus was designed to allow the initiation of the aggregation while the sample was on orbit.

Unfortunately, the accident on MIR occurred during the CGel flight. As a result, very little of the planned experiments were carried out on CGel. Virtually no scattering measurements could be performed because of the loss of power resources. Instead, Dave Wolfe, the astronaut, was able to take a series of high quality pictures of the CGel samples. These provided very intriguing information about the nature of the structures formed during the phase separation of the colloid-polymer mixtures when they are in the three phase region. The pictures suggest that the crystal phase forms within the fluid phase, and does not sublime from the solid phase. However, the magnification of the camera lens used for these photographs was not sufficient to confirm this unambiguously, and further experiments to determine this will have to await PCS-II. No scattering was done, so no data was obtained about the crystal structures formed. In addition, no experiments were performed with the fractal aggregates, as they required light scattering to perform any experiments what so ever.

A second flight of CGel is planned for Oct. 1998, on the John Glenn shuttle mission. However, because of the very short duration of the mission, and because we are sharing our glovebox experiment with a second flight of CDOT, there will be little time for experiments. In addition, there will be little time to allow binary crystal alloys to grow. As a result, the most critical part of the flight will be to test the formation of fractal aggregate gels initiated by mixing two solutions on orbit.

### 2.3.2 Ground-based work

A large research effort has been established to support the flight experiments in both the PI's labs. In Edinburgh, a post doc, Andy Schofield, has mastered the art and science of making PMMA particles which are essential for many of the experiments, and he now supplies samples for all ground based experiments at both Edinburgh and Harvard, as well as those performed at NASA GRC. He is also supplying all the flight samples. Because of the need to synthesize and then clean all samples, this is a large task.

In addition, at Edinburgh there is an active research effort investigating the phase behavior of mixtures of colloids and polymers. The initial focus was on the nature of the colloidal gel phase that is observed when a strong attraction is induced through the addition of a high concentration of polymer, and considerable progress has been made in understanding this [10,20]. Other work has involved the study of the phase behavior of the mixtures, particularly in the regions where two or three phases can coexist [9,11]. Much of the initial work has focused on scattering measurements, using static light scattering to obtain information about the structures of the different phases and dynamic light scattering to obtain information about their dynamics. While these experiments provide important insight into the properties of the different phases, data analysis becomes increasingly difficult as the phases are mixed together, since the light beam probes some combination of all three phases. Thus, light scattering measurements can provide very useful information about the dynamics of the phase separation process, but little information about the detailed kinetics within each individual phase. Therefore, an effort has begun to develop direct visualization of the colloidal particles using DIC microscopy. To fully develop this methodology, initial effort has been in its refinement through the study of the structure of monodisperse colloidal crystals.

Complimentary work is being carried out at Harvard, where Phil Segre, the project coordinator for PCS, has been conducting experiments to probe growth and dynamics of colloidal gels formed by colloid-polymer mixtures. Currently, this work is continued by Urs Gasser. This is being done to compare with the behavior of gels formed by irreversible aggregation of colloidal particles; both structures have similar fractal scaling on intermediate length scales, but the structure on shorter length scales, and the resultant elasticity of the networks, is expected to differ significantly since the colloid polymer mixtures are held together by bonds that do not resist rotation, and hence are much more susceptible to rearrangements than are the gels formed by irreversible aggregation, where the interparticle bonds are believed to be much less susceptible to rearrangements. Segre, and currently, Gasser is also carrying out experiments to complement those of Schofield further exploring phase boundaries of binary alloy colloidal crystals.

An important development that Segre has undertaken is to find a fluid, cycloheptyl bromide, that, when mixed with decalin, allows the PMMA particles to be both index matched and nearly buoyancy matched. With this fluid, it is possible to improve the buoyancy match of the particles by close to two decades in density difference, going from  $\Delta\rho \sim 0.25$  to  $\Delta\rho \sim 0.002$ . This reduces the effects of

sedimentation, allowing more detailed experiments to be performed on the ground. However, it is impossible to exactly buoyancy match the particles, and time-exposure video photography shows that crystals formed in this solvent still sediment. In addition, the use of this solvent does not eliminate convection effects. Finally, gravitational effects are actually essential to correctly and accurately determine the ratio of the phases and therefore determine where the sample is on the phase diagram. Similarly, to determine the volume fraction of the two colloids in the binary mixtures requires adjusting their respective volume fractions to the region of coexistence between fluid and crystal, and allowing the crystals to separate by sedimentation. Thus, the imprecise buoyancy match is essential for the sample preparation.

The near buoyancy match significantly extends the amount of ground-based preparatory research that can be done. Thus, Segre is exploring the dynamics of the crystallization of binary alloys using buoyancy matched mixtures to complement the work of Schofield in Edinburgh. In addition, Segre is using the buoyancy matched samples to study the dynamics of the gels. He has found that gels can form at much lower volume fractions using the near buoyancy match solvent, but these gels have a very unusual behavior. Their static scattering exhibits a peak at small angles, similar to that seen at higher volume fraction. This peak represents the correlations between the clusters that lead to the formation of the gel, and is seen in many different forms of colloidal gelation [19,21,22]. Surprisingly, however, for the low volume fractions colloid-polymer gels, the scattered light at this peak exhibits dynamics that are not arrested or non-ergodic [21], unlike the case of gels formed at higher  $\phi$ . In order for the light to be ergodic, the gel clusters must move over distances that are larger than their sizes; nevertheless, the structure of the gel persists. Segre is investigating this strange behavior.

## 2.4 Current Research

Much of the current research effort is associated with the preparations for the flight experiments. There is still one glovebox experiment that will fly in the fall of 1998. In addition, more data analysis is being carried out for the flights that have already taken place, primarily to attempt to learn as much as possible from the photographs, through the use of digital image enhancement.

Extensive work is also being carried out to assist NASA LeRC develop the PCS-I apparatus. The apparatus that will be used for PCS-I was originally scheduled to be identical to that flown in the PH<sup>A</sup>SE experiment by Chaikin and Russel, and hence the design and configuration of the experiments were determined to optimize both their work as well as that of PCS-I. Naturally, this lead to some compromises in the type of experiments that can be performed. However, the PH<sup>A</sup>SE apparatus was constructed on a very tight timetable; as a result there were several major components that did not perform properly. As a consequence, the apparatus is undergoing a major overhaul and is being completely redesigned for PCS-I. In addition to correcting the most serious problems encountered in PH<sup>A</sup>SE, a new probe is being added. This is a very small angle camera, which will allow both static and dynamic light scattering to be performed to angles as low as 0.3°. However, the main design of the apparatus remains unchanged. This will



allow the NASA design team to profit from everything learned in the PH<sup>A</sup>SE experiment, and should result in equipment that performs much better.

To assist in the construction of the apparatus, second post doc at Penn, Luca Cipelletti, is developing the new very small angle camera for light scattering. It will allow both static and dynamic light scattering to be performed at scattering angles down to  $0.3^\circ$ . This will be very valuable for the study of nucleation and growth of colloidal crystals, as the crystals themselves will scatter in the forward direction, allowing their growth to be monitored by measuring the small angle scattering. It will also be essential for the study of the properties of the colloidal aggregate gels. A new interpretation of the light scattering from these gels has been developed [22] which allows their elastic modulus to be determined from the dynamic light scattering providing the scattering is carried out at sufficiently low  $q$ ; the small angle dynamic camera will allow this to be accomplished. Cipelletti is developing this instrument and studying the behavior of fractal colloidal aggregate gels formed from the one material that can be nearly buoyancy matched to the solvent, polystyrene. Interestingly, his results suggest that even samples that are as well buoyancy matched as possible still apparently exhibit sedimentation which obscures the dynamics of interest.

The experiments that will be conducted on PCS-I address the behavior of bulk samples. The experimental tools available in the PCS-I apparatus are based primarily on light scattering. To study the structure of crystalline materials, there is a Bragg scattering camera that collects light scattered at angles from about  $7^\circ$  to nearly  $60^\circ$ . The source is a solid-state doubled YAG laser operating at 532 nm; thus the accessible angles correspond to scattering wave vectors from about  $2.4 \mu\text{m}^{-1}$  to  $20 \mu\text{m}^{-1}$ . The camera collects the scattered light over all azimuthal angles, and the laser illuminates a large sample volume. This is essential to ensure a good ensemble average to get good powder pattern data from crystallites, required for accurate identification of structures; in space, the crystals can grow to larger sizes, requiring more sample to be illuminated to obtain a good powder average. The second camera that collects light at very small angles. In the lab, it is able to collect light from  $0.3^\circ$  to about  $3^\circ$ , corresponding to scattering wave vectors of  $0.1 \mu\text{m}^{-1}$  to  $1.1 \mu\text{m}^{-1}$ , although this full range may not be achieved in the final flight instrument. This camera also collects light over the full azimuthal angles. Since the light is imaged directly onto the camera, the signal can be time averaged to determine the static scattering, or it can be correlated to determine the dynamic scattering. Importantly, the signals from all azimuthal angles around a single  $q$  can be averaged, providing much better statistics for very slow dynamics characteristic to such low  $q$ . This camera can also be used to study the time evolution of the static scattering at low angles, which directly probes the growth of crystals or droplets. For both of these cameras, the beam diameter is nearly 1 cm, and, since the sample cell thickness is about 1 cm, the illuminated volume is about 0.5 cc.

In addition to the two scattering cameras, there is a second doubled YAG laser which illuminates the sample from the side, and allows traditional dynamic and static light scattering to be performed. The detector is an avalanche photodiode, that is mounted on an arm that can be rotated, achieving scattering angles from about  $10^\circ$  to

160°, corresponding to scattering wave vectors from about  $3.5 \mu\text{m}^{-1}$  to about  $40 \mu\text{m}^{-1}$ . In this case a smaller sample volume is probed; however, this sample volume is restricted to the center of the cell, where the excitation and detection volumes overlap. In this case, ensemble averaging can only be achieved by rotating the cell. This samples different speckles, providing an ensemble average for light scattering; however, it does not provide an ensemble average over larger volumes of the sample.

Finally, there is also a color camera that images the samples with much lower magnification, allowing the more macroscopic behavior to be studied. This should provide some information on the overall crystal morphology, as well as serve as a check for the behavior of each cell.

The results of PCS-I should yield considerable information about the bulk properties of the samples. For the binary alloy colloidal crystals, we will learn about the crystallization kinetics, the morphology of the crystals, and their structures. We will gain some information about the phase behavior of binary alloys, although this will be severely limited by the small number of sample cells available. In addition, we will learn a great deal about the structure and dynamics of the crystals once they are formed as we will be able to do extensive light scattering measurements on them. The PCS-I apparatus will also be able to perform some simple rheological measurements; the cell will be rocked through a few degrees, and the scattered intensity will be measured. By finding the frequency with the largest response, it will be possible to determine the resonance frequency. Since the sample geometry is known, this can be used to calculate the speed of sound, and hence the shear modulus of the sample. Similarly, for the colloid polymer mixtures, we will learn a great deal about their phase behavior and the kinetics of their phase separation. We will be able to determine the structure of the colloidal crystals formed, and should be able to learn information about their dynamics. This information will again be restricted to only a few judiciously chosen mixtures.

The information obtained from PCS-I will be invaluable in determining the behavior and properties of these samples. However, it will be, by its very nature, limited in scope. Current plans call for three sample cells to contain samples that will form binary alloy colloidal crystals, and another three to contain samples that will contain colloid polymer mixtures; of these, two will contain gel samples, and the third will contain a sample near a critical point. The binary alloy mixtures will be chosen to produce examples of crystals in different structures, and will contain suitably adjusted mixtures of PMMA particles of different sizes. The colloid-polymer mixtures will focus on the dynamics of formation and the properties of the structures formed. However, they will be restricted to samples that form predominantly a single phase, as the interpretation of both the static and, more critically, the dynamic light scattering from samples with mixed phases is much more difficult and uncertain.

## **2.5 Proposed Experiments**

While the information obtained from PCS-I will be of great value, many questions will remain unanswered. Furthermore, to exploit the knowledge gained to create new

materials will require a second set of experiments. We propose to accomplish this in PCS-II.

The goals of PCS-II are to significantly extend the range of studies performed in PCS-I, and to use the knowledge gained to exploit “colloid engineering” to create new materials from colloidal precursors.

### 2.5.1 Binary Alloy Colloidal Crystals

The goal of PCS-II is two-fold. We wish to obtain more extensive information on the phase behavior of binary alloy colloidal crystals, and to perform more specific tests on the properties of the crystals themselves. In addition, we wish to exploit our ability to control their structure to synthesize new materials with the crystal structure of the binary alloy superlattices, and to perform detailed tests on these materials.

Studies of the phase behavior of the binary alloy crystals will require a larger number of samples with different size ratios,  $r$ , and sample volume fractions,  $\phi$ . Much of this can be done in ground-based testing in support of the experiment. Using nearly buoyancy matched samples will greatly assist this; for example, many crystal structures can take several months to grow on earth, and are currently only observable in an environment that has  $g \approx 0$ , which is achieved by slowly rotating the sample so the gravitational forces average to zero. However, this imposes large shear forces on the crystals, which can prevent their formation or modify their structure. Using the near buoyancy matched samples should alleviate some of these problems. However, this buoyancy match is not perfect, and over the extended period of the crystal growth, significant sedimentation will still occur; thus, there will inevitably be some tests that must be carried out in microgravity. In addition, we wish to study the properties of the crystals produced in much greater detail. The crystal structures of the binary alloys will be determined by the powder-average measurements performed in PCS-I. Therefore, rather than investigating a large number crystals to obtain an accurate powder average, in PCS-II, we will focus on individual crystals and study their properties. This will require different optics that will allow individual crystals to be probed.

This can be accomplished using a microscope. This will allow us to directly visualize individual crystals and determine their properties. The microscope can be set to both visualize the images of the crystals, and to collect light scattered from them. By combining the real and Fourier space probes of the crystals, we will be able to determine the orientation of the crystallites, and hence the direction of the scattering vector with respect to the crystal lattice structure. The combination of static scattering and direct imaging will provide detailed information about their structure. This is of particular value since their structures are so complex; it is not clear how precisely defined these structures are, given that the crystals are formed solely by entropy. The dynamic light scattering may allow us to measure the phonons in the crystals, and to determine their properties at different points in the Brillouin zone. This information will also be helpful in using these structures for materials synthesis. In addition, we plan to modify the structures and to investigate whether we can seed growth of specific crystals. We will do this by manipulating individual particles using laser tweezers. To accomplish this, we

may have to add a small number of particles with a different index of refraction, allowing them to be tweezed. By this means, we hope to learn considerably more about the properties and structure of the colloidal crystals, and to develop methods for enhancing the growth of large crystallites with a preferred orientation.

We also plan to make samples that contain particles that differ not only in size, but also in material. This will be the most ambitious implementation of colloid engineering. We will exploit our ability to modify the structure and morphology of the binary alloy crystals to tailor structures for optimum utility. We will focus on structures that exhibit novel optical properties, to take advantage of the light diffraction properties of these material. The exact materials that will be used will depend somewhat on the different suite of materials available which are compatible with colloid stability. Our current plans are to include mixtures of PMMA and silica as a model system. Both materials can be synthesized as very monodisperse particles and can have the same stabilizing polymer grafted to their surfaces, providing compatibility in the same solvent. In addition, the indices of refraction of the two materials are not too different, which should reduce problems of multiple scattering. However, they are sufficiently different that novel 3D grating structures should result, which should have interesting optical properties. An added advantage of using silica is that other materials can also be coated with silica [23,24], providing core shell particles that have a different core and a silica coating that is compatible with the PMMA.

Other materials which we will consider include metallic and semiconductor particles. Metallic particles, such as gold, have a strong optical plasma resonance, making them good candidates as interesting optical filters if this plasma resonance is combined with the ordering on the optical wavelength and the reduction in the surrounding optical phase space that ensues if the particles are inserted inside the superlattice formed by a second set of particles. Similarly, semiconductor particles can have important optical properties and these will also be modified by the superlattice.

It will be extremely difficult to crystallize any of these mixed systems in ground-based experiments. Because the particles are of different materials, and have different densities, the samples can not be buoyancy matched at all; moreover, differential sedimentation of the two different colloidal particles will prevent crystallization. Thus, virtually all the studies of the binary alloy crystallization of these mixed materials will have to be performed in microgravity during PCS-II. The phase behavior of these materials can be determined by analogy to the behavior of PMMA samples; while this will provide critical guidance, it will not provide complete information, as interactions of mixed particles may be slightly different from those of the same material, modifying the phase behavior in small but important ways. As a result, a larger number of samples will have to be studied in microgravity to determine where in phase space crystals form.

Once formed, light scattering in a traditional cell may be very difficult for determination of the structure. Since there will be two different materials present, it will not be possible to match the index of refraction of the solvent to reduce the scattering. As a result, these materials will have to be studied in relatively compact cells to reduce the total scattering. Alternatively advanced optical microscopy techniques will have to be

employed. For example, confocal microscopy, which allows visualization in more turbid or scattering media, could be very useful for imaging the details of the structures within the crystals. In addition, fluorescence microscopy could be used to isolate one of the colloidal particles which could be made so that it contains a dye that can be observed through its fluorescence. Thus, the ideal experimental tool here is a microscope.

Once these samples are formed, another class of experiment that we plan to perform is the local modification of their structure through the manipulation of individual particles using laser tweezers. This will provide new opportunities to develop even more interesting structures. For example, one of the most interesting features of photonic band gap structures is their influence on emitters embedded within the crystal. Because the phase space is restricted, the emission properties will be dramatically modified; both the lifetime and the frequency of the emission should be changed [8]. The effect should persist, albeit in a reduced fashion, if the reduction of the phase space that results from the grating is incomplete, as may be the case with some of the colloid-based materials. Nevertheless, even if phase space is not totally restricted, in that the stop bands do not extend in all directions, modification in the optical properties should still be pronounced. In addition, the behavior of localized defects in the structure will be analogous to dopants in traditional crystals, and will introduce new optical properties [6]. In order to create these localized structures, we will manipulate the individual particles that make up the binary alloy using laser tweezers.

We also plan to form colloidal crystal structures from particles that contain nematic liquid crystals within them. These may be monodisperse emulsion droplets, which have been successfully made into colloidal crystals at Penn, or they may be colloidal particles that are filled with liquid crystal. There has been one report about these materials in the literature, and we are attempting to obtain some of them. The unique feature of these particles is that the orientation of the nematic director can be changed with the application of an external electric field. This will dramatically change the optical properties of these droplets, offering intriguing additional control over their behavior.

### 2.5.2 Colloid-Polymer Mixtures

One of the most interesting features of the colloid-polymer phase diagrams are the regions of coexistence between several different phases, particularly near a critical point in their phase diagram. This regime has not been extensively studied in ground based experiments, since the phase diagram is determined by allowing gravity to separate the phases and thereby determine the amounts of each phase; the gas phase, with the lowest particle concentration, creams to the top, the liquid phase, with an intermediate particle concentration, settles in the middle, while the solid phase, with the highest particle concentration, sinks to the bottom. However, as the photographs from the CGel experiment highlighted, the structures that do form can provide considerable information about the kinetics of the phase separation and the coexisting states.

Some of the most important questions arise from the study of the fluid phase. For example, it is not clear whether fluid drops are formed in all cases upon phase separation. If they are, it would be very interesting to determine their surface tension, as it must play

a critical role in their formation. This could be done through a study of the shape of the droplets and a determination of the surface fluctuations. In addition, it would be very interesting to determine the dynamics of the liquid within the droplets, which could be done by dynamic light scattering, provided a single droplet could be isolated in the collection volume. It would also be interesting to determine the nature of the crystallization when a solid is present. The crystals may first form in the liquid droplets, and if this is the case, they should markedly modify the nature of the fluid within the drops. Alternatively, they may also sublime from the gas phase. Resolution of these questions may lead to finer control over the crystal structures that form, improving their potential uses for engineering new materials.

To study these effects, it is essential to be able to isolate the individual components. This can be accomplished by imaging the sample to identify the structures; they can also then be studied to determine effects such as where crystals form, and how the shape of the fluid droplets fluctuate. However, once the structures are isolated, it will also be important to use scattering techniques to increase our knowledge of their properties. For example, dynamic light scattering can provide critical information about the interparticle interactions within the fluid droplets. It can also provide some insight into the properties of the crystallites. Similarly, the structure of the crystallites is most easily determined through Bragg scattering. However, in all cases, it is essential that only a single component be present in the scattering volume; otherwise the interpretation of the scattered intensity is greatly complicated. The ideal method to achieve this would be through the use of a microscope, which allows very small volumes to be imaged and can also be adapted to allow scattered light to be collected from this same volume.

An additional advantage of using a microscope is that the particles can be manipulated with laser tweezers. Thus, for example, single particles could be organized into certain lattices with liquid droplets, forming well-defined nucleation centers for the further growth of crystals. In addition, for weak fluid droplets, the boundaries could be directly excited by moving particles near their interfaces with the laser tweezers.

### 2.5.3 Main Experimental Requirements

The most useful experimental tool for conducting all the proposed experiments is an optical microscope. A microscope could be configured to allow samples to be directly visualized using different types of optical imaging, including bright field, DIC and phase contrast, enabling the individual colloidal particles to be seen if they are large enough, and the nature of the structure formed to be observed, including the morphology of the binary alloy crystals, and the shape of the liquid droplets in the colloid-polymer mixtures. Additional information could be obtained by fluorescence microscopy through the judicious labeling of different phases using appropriate dyes. The microscope could also be configured to allow simultaneous light scattering from the samples, both dynamic and static. This would have the advantage of allowing the light scattered from very small volumes to be collected, enabling small, isolated structures to be probed without the contribution from neighboring structures. In addition, the microscope would allow some direct manipulation of individual particles, providing further control over the nature of the structures that are produced. Finally, the sample sizes required for microscopy are

very small, allowing a much larger number of samples to be studied in a single flight; this is essential to enable exploration of the broad phase space of these colloidal materials .

## **2.6 Current Research in Support of Proposed Experiments**

Considerable work is currently being carried out to develop experimental techniques that use an optical microscope for the study of colloidal particle samples. In Edinburgh, research is being conducted to use real space imaging of colloidal particles to determine crystal structure and the defects within. At Penn, and at Harvard now, there is extensive development of optical microscopes to perform other measurements. A microscope has been adapted to simultaneously image the sample and scatter from the sample, allowing both static and dynamic light scattering to be collected. A second microscope is used extensively to do fluorescence imaging to develop the required ability to label different particles or regions with dye molecules. Laser tweezers have been constructed in a neighboring lab, and are being assembled onto the scattering microscope. In addition, a commercial confocal microscope is being used to study the structure and dynamics of colloidal particles.

Other research is being carried out to learn how to synthesize new particles. In Edinburgh, Schofield is developing the synthesis routes required to make silica particles that are compatible with the PMMA particles. He is also exploring putting dye molecules into both PMMA and silica particles both for confocal and for fluorescent microscopy. At Penn, and at Harvard now,, research is being conducted in the synthesis of highly monodisperse emulsion droplets. Although this can be done with the usual fractionation techniques [11], this is not feasible when a very expensive material, such as a liquid crystal, is used in the interior. Thus new methods are being developed that require the use of much smaller quantities, making it feasible to synthesize the required material.

## **2.7 Anticipated Advance in the State of the Art**

Addressing the questions proposed above would significantly increase our understanding of the properties and behavior of colloidal suspensions. In addition, they would provide crucial guidance in the use of colloidal precursors for materials synthesis, and would help establish colloid engineering as a new synthesis route. The materials produced would also have unusual properties, that have not yet been fully anticipated.

# **3 Justification for Conducting the Experiment in Space**

## **3.1 Limitations of Ground-Based Testing**

The primary limitation with ground-based work results from sedimentation. A second less critical problem arises due to convection effects, which are also gravity induced. Both of these effects will be greatly reduced in microgravity. A basic understanding of the limitations imposed by gravity comes from the problems encountered in current experiments. We review these first, and then discuss more detailed estimates of the effects of gravity, even in the optimum case.

Experiments in Edinburgh probe the formation and structure of crystals from monodisperse colloidal particles using microscopy. They use small capillary tubes as sample cells; these are about 2 mm wide and about 100  $\mu\text{m}$  thick. These samples are loaded in a fluid state, the cell is sealed and the measurements begun. In the course of about an hour, the samples crystallize. The crystallization process is studied and the final structures are determined by imaging. However, during the course of the experiment, it is inevitably noticed that the particles sediment, so that the top of the cell has a lower density, which typically remains fluid, while the bottom has a higher density, where the crystals form. Thus, it is impossible to accurately set the volume fraction. Moreover, the sample at the bottom is always under the additional osmotic pressure of the sample above; this has a direct effect on its properties. In addition, as shown by the results of the CDOT experiment by Chaikin and Russel, the morphology of the crystals is significantly modified by the gravity-induced settling. This limits the size of the crystals that grow, which will place a significant limitation on their use for materials growth.

Experiments conducted by Segre at Penn and at Harvard also highlight the effects of gravity. He used time lapse video to record the formation and growth of the crystals from larger scale samples, again of monodisperse particles. He first used the standard mixture of index-matching fluids, tetralin and decalin, for which there is a density mismatch of  $\Delta\rho \sim 0.25$ . He observed the crystals to sediment quite rapidly. He then repeated the experiment using cycloheptyl bromide, which can be used to achieve a more nearly buoyancy matched sample while still index matching the PMMA. He estimated that the density mismatch was decreased by about two orders of magnitude, to  $\Delta\rho \sim 0.002$  (this is probably an optimistic estimate, with the actual density match being poorer); however, while the sedimentation velocity was reduced, and the crystals were larger and more dendritic, they also clearly continued to sediment. Because of uncertainties in mixing volumes, it is unlikely that density matching closer than this can be achieved; differences in thermal expansions also limit the exact buoyancy match. In addition, the only way to reliably and accurately set the volume fraction of the samples is to take advantage of their phase behavior. Their volume fraction can be adjusted to be in the two-phase region, with  $\phi$  between 0.5 and 0.55, where both the fluid and crystal coexist. The fluid has  $\phi = 0.5$ , while the solid has  $\phi = 0.55$ ; by allowing the denser crystals to sediment to the bottom of the sample, the volume fraction of the supernatant fluid is set exactly at  $\phi = 0.5$ . Accurate adjustment of the volume fraction is essential for all experiments, and this is the only reliable and accurate way of doing this. Thus, even the slow sedimentation of the buoyancy matched samples is highly desirable.

A final observation about gravity induced effects comes from some of the results obtained in the CGel glovebox experiment. In this experiment, samples remained in microgravity for about 4 months, when they were photographed. Although the results are not entirely certain, since no light scattering was performed, some of the pictures seem to show a noticeable difference in apparent photographic density from the top to the bottom of the cell. While it is not entirely certain, one explanation for this observation is that the material had sedimented slightly during the course of the experiment. Thus, it may actually be desirable to use buoyancy matched particles in the microgravity experiments



to completely eliminate this for the most delicate of samples and the longest duration experiments.

For PCS-II, the experiments where sedimentation effects will be most critical and the experiments will have the longest duration are probably the colloid-polymer mixtures. For these samples, the structure formed, particularly the liquid droplets, will be most susceptible to sedimentation. In particular, studies of their shape fluctuations to measure the effective surface tension will demand that there are no other effects that dominate, and will require very precise buoyancy matching. By contrast, the binary alloy colloidal crystals will not be able to be matched at all, and will absolutely depend on microgravity to form. However, our experience with the glovebox experiments has already shown that we are able to form good AB<sub>13</sub> crystals from PMMA in microgravity, making it highly likely that we will be able to reproduce this using the new materials proposed here.

We can make several estimates of the effects of gravity on the crystals. The first one is to calculate when sedimentation can compete with diffusion for the growth of the crystals. The concept here is that a free crystal grows by diffusion of the accreting particles to the surface. Competing with this is the sedimentation of the whole crystal. We can estimate an effective Peclet number,  $Pe_{eff}$ , which expresses the ratio of the time for a single particle to diffuse its own size,  $t_D$ , to the time for the crystal to sediment a single particle size,  $t_C$ . We might expect that when  $Pe_{eff} = t_D/t_C \sim 1$ , the effects of sedimentation will become significant. This will allow us to estimate a maximum crystal size that can be achieved. We do this for crystals from monodisperse particles as all the required parameters are known for them.

The buoyant mass of a crystal of typical radius  $R_C$  is given by

$$m_b = 8\Delta\rho_p\Delta\rho R_c^3 \quad (1)$$

where  $\Delta\rho_p = 0.05$  is the difference in particle density between the crystal and the fluid, while  $\Delta\rho$  is the intrinsic difference in density between the particles and the surrounding fluid. The sedimentation velocity can then be calculated by balancing the gravitational force on the crystal with the Stokes drag of the fluid, resulting in

$$v_C = \frac{\Delta\rho_p\Delta\rho g R_C^2}{6\pi\eta} \quad (2)$$

where  $g$  is the gravitational acceleration constant and  $\eta$  is the viscosity of the surrounding fluid, which we take to be the value of the viscosity of the fluid phase which is about 50 times that of the solvent. The characteristic times are then

$$t_C = \frac{R}{v_C} \quad (3)$$

and

$$t_D = \frac{R^2}{D} \quad (4)$$

where  $D$  is the diffusion coefficient of the single particles, which we calculate using the Stokes-Einstein relation,

$$D = \frac{k_B T}{6\pi\eta R} \quad (5)$$

where  $T$  is the temperature and  $k_B$  is Boltzmann's constant. This allows us to calculate the effective Peclet number for this form of crystal growth,

$$Pe_{eff} = \frac{8\Delta\rho_p \Delta\rho R_C^2 R^2 g}{k_B T}. \quad (6)$$

If we use  $Pe_{eff} = 1$  as a criterion for when sedimentation becomes important, we can determine the maximum crystal size that can grow under different conditions,

$$R_{C,max} = \sqrt{\frac{k_B T}{8\Delta\rho_p \Delta\rho g R^2}} \cup \frac{3 \times 10^{-7}}{\sqrt{\Delta\rho g}} \text{ cm} \quad (7)$$

using CGS units. If we use  $R = 0.5 \mu\text{m}$ , we can calculate the size of PMMA crystals that can be formed on earth with the standard index matching solvents, decalin and tetralin, for which  $\Delta\rho \cup 0.25 \text{ gm/cc}$  and  $g \cup 10^3 \text{ cm/sec}^2$ . We obtain a value of  $R_{C,max} \sim 4 \mu\text{m}$ ; this is consistent with the observation that dendritic crystals are never observed on earth. The value of  $R_{C,max}$  varies inversely as the square root of both  $g$  and  $\Delta\rho$ , allowing us to estimate the effects of both buoyancy matching a microgravity. If we improve the buoyancy match by two orders of magnitude, the size of the crystals will increase by one order of magnitude to  $R_{C,max} \sim 40 \mu\text{m}$ . By comparison using the standard non-buoyancy matched fluids, but doing the experiment in microgravity gains an additional 3 decades, to crystals of about  $R_{C,max} \sim 4 \text{ mm}$ , again consistent with what is seen in the CDOT experiments. Combining the buoyancy match and microgravity will produce crystals of remarkable sizes,  $R_{C,max} \sim 4 \text{ cm}$ !

Of course, these are the simplest cases to consider. However, it also gives us guidance for the binary alloys. The key is the square root dependence on both  $\Delta\rho$  and  $g$ . Thus even a far less favorable density mismatch of 20 would decrease the size of the crystals by a factor of 10, while microgravity would still provide a benefit of three decades. As a result, we might estimate  $R_{C,max} \sim 400 \mu\text{m}$  in the most unfavorable case of binary alloys with a large density mismatch, provided we do the experiment in microgravity. This size is still quite reasonable for making materials with interesting optical properties.

Finally, it is also interesting to estimate the actual sedimentation velocity for some cases. It is given by Eq. (2), and for a  $100\text{ }\mu\text{m}$  crystal of PMMA in decalin and tetralin in microgravity,  $v_C \sim 0.5\text{ }\mu\text{m/sec}$  on earth, where we have assumed that  $\eta = 1$  Poise. In microgravity, this is reduced by six decades, becoming more like about  $v_C \sim 1\text{ }\mu\text{m/month}$ . For binary alloy colloidal crystals, this value might increase to several  $\mu\text{m/month}$ . This should be tolerable in performing these experiments.

In evaluating the significance of these calculations, we feel that the estimates for the monodisperse PMMA crystals are probably most relevant to the colloid-polymer mixtures, while estimates for the binary alloys should use the large density mismatches calculations above. The exact value of the density mismatch will depend on the materials chosen; however representative values are silica:  $\Delta\rho \sim 1.3\text{ gm/cc}$  and gold:  $\Delta\rho \sim 17\text{ gm/cc}$  and these values were used above.

### **3.2 Limitations of Drop Towers**

The length of time for formation of any of these structures is far too long for short term microgravity experiments, such as those performed in a drop tower or in an airplane. In a drop tower, low gravity is achieved only for a few second. The growth of binary colloid alloy crystals can take weeks to months on earth; it may be more rapid in microgravity, but will still take several weeks. Similarly, the phase separation of colloid-polymer mixtures can take several minutes to many days. It also is much too slow for a drop tower or an airplane.

### **3.3 Limitations of Testing in Aircraft**

The length of time for formation of any of these structures is far too long for short term microgravity experiments, such as those performed in a drop tower or in an airplane. In airplane, low gravity is achieved only for less than a minute. The growth of binary colloid alloy crystals can take weeks to months on earth; it may be more rapid in microgravity, but will still take several weeks. Similarly, the phase separation of colloid-polymer mixtures can take several minutes to many days. It also is much too slow for a drop tower or an airplane.

### **3.4 Need for Accommodations on the Space Station**

The space station provides an environment where microgravity is sustained long enough to allow these experiments to be conducted. The samples can be homogenized by mixing them and then can be allowed to develop under microgravity for an extended period of time. Their structure and properties can then be probed in situ allowing the unique behavior of the new materials to be studied.

### **3.5 Limitations of Mathematical Modeling**

The phase behavior of binary alloy colloidal crystals has been calculated, primarily using maximum packing considerations. However, while these calculations are a useful guide for experiment, they tend not to be in direct agreement with the experimental results. Thus, further experiment will provide additional guidance for further refinement of the theory.

Theoretical calculations of the optical properties of a variety of structures have also been calculated. However, these calculations are quite difficult and can not be done analytically. As a result, they tend to focus on structures that can be easily fabricated, and have not, as yet, been performed for binary alloy colloidal crystals. While these would be useful, they are not essential for performing the experiments. The experimental results obtained should be very helpful in directing any future modeling. They will provide the essential experimental input that is critical to test new models.

### **3.6 Limitations of Other Modeling Approaches**

Other modeling is rudimentary or non-existent. The experiments proposed here will provide the definitive data to allow further modeling to be carried out.

## **4 Experimental Details**

### **4.1 Experiment Procedures to be Used for PCS-II**

#### **4.1.1 Binary Alloy Colloidal Crystals**

The samples will consist of polymethylmethacrylate (PMMA) particles, stabilized by a thin coating of poly-12-hydroxystearic acid. Either the core or the whole particles will be labeled with a fluorescent dye such as rhodamine in order to make the particles visible with fluorescence microscopy. The solvent will be a mixture of decalin and tetralin and possibly other chemicals to exactly match the index of refraction of the PMMA. The choice of the size ratio, particle concentration ratio and total particle volume fraction will be based on the results of the preliminary glovebox experiments and ground-based investigations of the phase diagram, supplemented by the results of PCS-I. Once in orbit, the samples will be homogenized by shear melting with a magnetic stir bar.

Similar samples will have been investigated in PCS-I by light scattering. Therefore the results from PCS-I will be a great help for choosing the size ratios and the volume fractions of the samples to be studied in PCS-II. While PCS-I is designed to observe an ensemble of many crystallites in order to obtain information about the growth of an average crystallite, it will be possible in PCS-II to study the formation and growth of a single crystallite. This is complementary to PCS-I, and it will provide new insights to the crystallization process, that will complete the knowledge from the earlier ground- and space-based experiments.

Once the sample is homogenized, the nucleation and growth of individual crystallites of the binary colloidal alloy will be monitored with the confocal microscope, by taking three dimensional stacks of images. The distance between two images will be smaller than the particle diameter in order to make an accurate determination of the particle positions possible. To get a good time resolution, such three dimensional stacks of images will be taken as fast as the instrument allows it. Confocal microscopy will allow to make observations about the shape and the structure of the nuclei that are not possible with the light scattering techniques used in PCS-I, since not only the average structure of the nuclei but also its variations within a nucleus can be studied. This is of interest since it is likely that the core and the surface of the nuclei do not have the same structure. Furthermore, the structure of the nuclei may change as they become bigger. In the extreme case the nucleation might even take place via a structure that is different from the bulk solid phase. Compared to the growth of monodisperse crystals the growth process in binary systems is likely to differ because the two particle species have to be ordered on the surface of the crystal. In PCS-II it will be possible to observe this process by tracking individual particles while they are incorporated into the crystal lattice.

The shape of the nuclei will reveal information about the way the crystals grow in micro-gravity. The crystallites might grow fast in certain crystallographic directions which could give them a layer like structure. Also their shape will give some hints about the processes that limit the growth. For face-limited growth the nuclei are expected to be roundish while fast diffusion limited growth is expected to result in edgy or fractal like shapes. The comparison with analogous ground-based experiments will reveal differences in the growth behavior under micro-gravity.

Series of two dimensional pictures taken in fast succession will allow to track all visible particles. This will be done either by video microscopy or with the confocal. It allows to characterize the way how particles move and diffuse in the sample.

Once large crystallites have formed we will investigate the properties of the crystal lattice. Again the structure of the stable structure can be determined by taking 3D stacks of images with the confocal. In order to measure the elastic properties, a test bead within a crystallite can be grabbed with laser tweezers and be used to distort the lattice. The bead is vibrated back and forth with the laser tweezers in order to create collective excitations (the equivalent of phonons) that are then observed by video- or confocal microscopy. Micro rheology will be used to find the elastic properties in the linear regime. In order to do this the motion of a particular bead will be tracked. This can be done by either confocal or video microscopy.

The laser tweezers will also be used to modify the crystal lattice by creating defects.

#### 4.1.2 Colloid-Polymer Mixtures

The colloidal particles for this experiment will again be dyed PMMA spheres suspended in an index matched fluid. The volume fractions of these samples will range

from about 1% to 30%. The polymer will be polystyrene, with a molecular weight ranging from about 100,000 to 1,000,000.

The colloid-polymer mixtures will be homogenized using the same procedure used for the binary colloid mixtures. After they are homogenized, the formation of the gel will be monitored by taking 3D stacks of images in the same way as for the binary colloidal crystals.

During the equilibration of the samples, DIC or phase contrast microscopy (and occasionally also confocal microscopy) will be used to find out which samples will eventually contain gas, liquid or solid or a combination of these. An automatic recognition of the different phases could save a lot of time. This information will be used to establish the phase diagram of this system under micro-gravity, and it will be the input for selecting a set of representative samples that will be studied in more detail. Also this will complete the insight gained from PCS-I into the mechanisms that lead to the ultimate equilibration of the gel. The selected samples will be observed in longer confocal or video-microscopy runs in order to characterize the present structures and the different phases. Colloidal crystals may form in one of the phases. Since they can form at low volume fractions and result from an attractive interaction between the particles, their growth and evolution may be significantly different from the formation of those formed by hard spheres. Therefore, we will use confocal microscopy to study their nucleation and growth in a way that is analogous to the one described in the section above about binary colloidal crystals.

In addition, some samples will contain test beads that will be used for micro rheology measurements, and the elastic properties of the gels and solid structures will be measured with laser tweezers (rheology).

#### 4.1.3 Colloid-Metal, Col.-Semiconductor, and Col.-Liquid-Crystal Mixtures

The phase diagrams of samples made of colloid-metal, colloid-semiconductor, and colloid-liquid-crystal mixtures are expected to be similar to the case of binary PMMA mixtures. However, this is difficult to test in ground based experiments, since these samples cannot be density matched by choosing a suitable solvent. Therefore, it will be part of the experiments planned for PCS-II to map out the details of the phase diagrams of the different sample types.

The experiments needed to study the formation and the evolution of the structures in these samples will be analogous to the ones described in the sections on binary alloy colloidal crystals and colloid-polymer mixtures above. In addition the effect of dc- and ac-electric fields on the optical properties of these samples will be determined. In order to do this a sample will be illuminated with monochromatic light under various angles during a video microscopy run.

## 4.2 Measurements Required

### 4.2.1 Binary Alloy Colloidal Crystals

Nucleation and growth:

- Homogenization by strong shearing
- Long time series (up to several hours) of 3D images taken with the confocal
- Time series of 2D images (video microscopy or confocal)

Structure determination:

- Time series of 3D images taken with the confocal
- DIC or phase contrast microscopy for the large scale structure
- Modification of crystal lattices with laser tweezers (confocal or video microscopy)

### 4.2.2 Colloid-Polymer Mixtures

Growth of gel-like structure:

- Homogenization by strong shearing
- Long time series (up to several hours) of 3D images taken with the confocal
- Time series of 2D images (video microscopy or confocal)

Properties of gel-like structure:

- Micro rheology with test beads (confocal or video microscopy)
- Rheology using laser tweezers with confocal or video microscopy
- Time series of 3D images taken with the confocal
- Time series of 2D images (video microscopy or confocal)

Equilibration of gel-like structure:

- Regular short observation by DIC, phase contrast or confocal microscopy

### 4.2.3 Colloid-Metal, Col.-Semiconductor, and Col.-Liquid-Crystal Mixtures

Nucleation and growth:

- Homogenization by strong shearing
- Long time series of 3D images taken with the confocal
- Time series of 2D images (video microscopy or confocal)

Structure determination:

- Time series of 3D images taken with the confocal
- DIC or phase contrast microscopy for the large scale structure
- Modification of crystal lattices with laser tweezers (confocal or video microscopy)

Determination of optical properties:

- Application of a dc- or ac-electric field and illumination with monochromatic light during video microscopy runs

### **4.3 Test Plan including Ground Characterization of Flight Hardware**

Ground based experiments are currently underway to support PCS-II as well as PCS-I. For the binary colloidal crystal alloys, we have fabricated a supply of PMMA particles, that can be dyed for experiments using fluorescence microscopy. Also, experiments with systems containing liquid crystal droplets are underway. Their phase behavior should be similar to that of PMMA, although this will be tested to determine any differences. However, their optical properties can be controlled by an externally applied electric field which will align the liquid crystal molecules in the droplets and change their scattering properties. Other potential new particles will also be explored.

Experiments now underway in the laboratory will provide a data base on imaging of various types of samples with confocal and video microscopy (monodisperse and binary PMMA samples, PMMA-polymer samples, liquid crystal droplets). PCS-I and the ground based experiments will show which particle diameter ratios and volume fractions for the various sample types will be most promising for the colloidal engineering experiments of PCS-II. Also, experiments using laser tweezers for rheology, modification of crystal lattices and pattern formation are planned.

To ensure that the optimum information can be obtained from the space experiment, it will be essential to have a model of the apparatus available to the PI's. This will allow testing of the experimental procedure and will enable the PI's to learn all the inevitable idiosyncrasies of the apparatus. The apparatus should be available for at least six months, if possible.

### **4.4 Specific Analysis Required**

Major parts of the software that will be necessary for data analysis exist already and are used routinely for the data analysis of ongoing ground based experiments. In particular this includes software for image analysis and particle recognition as well as software for the recognition and structure analysis of colloidal crystals.

### **4.5 Preflight Experiment Planned**

All experiments that are planned for PCS-II will also be done before the flight, either with inverted microscopes or on the flight instrument. More details about preflight experiments are given in section 4.3 above.

### **4.6 Post Flight Data Handling and Analysis**

The same form of data analysis will be used after the flight as is used during the flight. Additional software that is required for data analysis will be purchased or written by the principal investigator team.

The post-flight data analysis will require that the PI's have access to as much of the raw data collected during the flight as possible.



#### **4.7 Mathematical Models Used**

Well-accepted mathematical models representing the physics of fluid mechanics, volume fraction fluctuations, and brownian motion will be the basis for data analysis.

The experimental results may serve as a guide for developing new mathematical models.

#### **4.8 Application of Results**

The major result obtained from the planned experiments will be that the most promising routes to be followed for fabricating new materials with desirable properties through "colloid engineering" using entropically controlled crystallization will be identified. E.g. this could be of great interest for the production of novel optical filters or photonic band gap materials.

In addition there will be a great increase in our knowledge of the phase behavior of mixtures of colloidal particles of different types, especially for the samples that cannot be density matched. Also, new insight into the crystal structures that are formed by alloys of colloidal particles as well as the kinetics of their growth and the dynamics and properties of the structures formed will be gained.

### **5 Experimental Requirements for PCS-2**

The following sections contain specific requirements necessary in order to fulfill the science mission for PCS-2 (the Physics of Colloids in Space-2).

#### **5.1 Sample Description**

Binary alloys and colloid-polymer samples will be used for these experiments. The PI will provide all these samples for the ground tests and flight experiments. The PI will assure sample quality, cleanliness, and suitability/compatibility for examination over the wavelength range of experimentations.

##### **5.1.1 Binary Alloys**

Several different sets of samples will be used. A complete set of samples made entirely of PMMA will be included as a test case. The behavior of these can be studied on the ground, and compared directly to that in microgravity. All the other samples will be completely new in that they will consist of particles made from different materials. It will not be possible to study these on the ground at all, due to differential sedimentation; as a result, it will be necessary to explore the full phase space of these samples during the flight, which will require more samples. Fortunately, the volume of each sample is so small that this is feasible. The essential requirement for the particles is that they remain stable against aggregation once they are mixed together. This will be tested on the ground.

In some samples, a rhodamine fluorescent dye will be added to allow imaging by confocal microscopy, which may be the only way to image these materials.

Other samples will have additional probe particles that can be manipulated with laser tweezers. Refractive index differences,  $\Delta n$ , of around 0.2 will be used.

#### 5.1.2 Colloid-Polymer Mixtures

These will be exclusively PMMA in index matched solvents. In some samples, a rhodamine fluorescent dye will be added to allow imaging by fluorescence microscopy. Other samples will have additional probe particles that can be manipulated with laser tweezers. Refractive index differences,  $\Delta n$ , of around 0.2 will be used.

### 5.2 Sample Cell and Light Microscopy Apparatus Requirements

The sample cell and flight instrument shall have the capability for:

#### 5.2.1 Sample Homogenization

Homogenization shall be sufficient to “melt” the colloidal sample and disperse any existing crystallization. Homogenization and video microscopy are required simultaneously, or within 1 minute after mixing. Homogenization of individual samples is required (e.g. - when studying nucleation and growth).

#### 5.2.2 Optical Imaging

High magnification, high resolution visual imaging of both highly index matched (to 0.001) and fluorescent colloidal particles (nominally 0.01-5.0  $\mu\text{m}$ -sized) is required with a field of view ranging from 100 $\mu\text{m}$  x 100 $\mu\text{m}$  up to the width of the sample cells. At least 256:1 (8-bits) of dynamic range is required for these measurements. Particle centroid resolution of 5nm is required in all three directions. The resolution depth shall be up to 75  $\mu\text{m}$  into a sample of 0.1 optical density. Temperature stability of 0.1 C is required over the duration of the measurements. High resolution color images are required at frame rates up to 30 Hz. This is needed to enable the quantitative study and measurement of colloidal nucleation and growth, structure, and dynamics.

#### 5.2.3 Confocal Microscopy

High magnification, high contrast three-dimensional visual imaging of highly index matched, highly non-index matched, and fluorescent colloidal particles (nominally 0.01-5.0  $\mu\text{m}$ -sized) is required with a field of view ranging from 100 $\mu\text{m}$  x 100 $\mu\text{m}$  up to the width of the sample cells. At least 256:1 (8-bits) of dynamic range is required for these measurements. Particle centroid resolution of 5nm is required in all three directions. The resolution depth shall be up to 75  $\mu\text{m}$  into a sample of 0.1 optical density. Temperature stability of 0.1 C is required over the duration of the measurements. High resolution images are required at frame rates up to 30 Hz. This is needed to enable the visualization, and quantitative measurement of the colloidal 3-dimensional structures.

*Given adequate time and resources the following two techniques (5.2.4 DLS, and 5.2.4 SLS) would provide important complementary science. Multiangle Static and Dynamic Light Scattering through the microscope with variable width incident beam to illuminate from 10 microns to 1 mm of the sample While not a requirement we would like to use these capabilities if they become available. These are direct Fourier space probes which allow a tremendous advantage in averaging over a much larger number of particles than the real space techniques (i.e. confocal microscopy). Thus they will provide considerably more information in the same amount of time. And they will reduce the data storage requirements by many orders of magnitude.*

#### *5.2.4 Dynamic Light Scattering*

*Measurement of scattered light intensity with time,  $I(q,t)$ , from  $5^\circ \leq \theta < 175^\circ$ , with a 0.25 degree resolution, is required. The laser beam shall have an adjustable power level and be collimated at the sample, with a diffraction limited spot having a spot size adjustable in diameter from 5 to 600  $\mu\text{m}$ . The beam incident power shall be measured to an accuracy and precision of  $\leq 1$  percent. The beam stability shall be better than 0.1% and beam polarization shall be linear and  $\geq 500:1$ . Temperature stability of 0.1 C is required over the duration of the measurements. Autocorrelation of either detector photon counts or electric current is required, over delay times from 25 nanoseconds to 10000 seconds. This measurement is needed to enable the quantitative measurement of dynamics from localized regions within the colloid sample.*

#### *5.2.5 Static Light Scattering*

*Measurement of the scattered light intensity,  $I(q)$ , from  $5^\circ \leq \theta < 175^\circ$ , with a 0.25 degree resolution, is required. 4096:1 (12-bits) of dynamic range is required for these measurements; the intensity measurement shall have an accuracy of  $\leq 0.1\%$  of full dynamic range. The laser beam shall have an adjustable power level and be collimated at the sample, with a diffraction limited spot having a spot size adjustable in diameter from 5 to 600  $\mu\text{m}$ . The absolute beam incident power shall be measured to an accuracy and precision of  $\leq 1$  percent. The relative beam stability shall be 0.1% and the incident beam polarization shall be linear and  $\geq 500:1$ . Optical flare shall be minimized so as to allow measurement of form factors of dilute polystyrene particles down to 5 degrees scattering angle. Temperature stability of 0.1 C is required over the duration of the measurements. High resolution black and white images are required at frame rates of up to 30 Hz over a period of up to 30 seconds per sample (with sequential images taken using log-spaced time increments after the first 30 seconds of 30 Hz images). This measurement will be used to quantify colloidal nucleation and growth, as well as structure.*

### 5.2.6 Laser Tweezers

Performing single particle manipulation of either a bulk colloidal sample particle, or a particle of a much higher refractive index contrast (e.g. a particle with refractive index,  $n=1.59$  in a solution of  $n=1.5$ ) having the same or different sizes from the bulk colloid by displacing the particle out of its equilibrium position by up to  $20\text{ }\mu\text{m}$  is required. Visualization of the directed beam is required. The sample cell and apparatus shall be capable of performing high magnification imaging (5.2.2) or confocal microscopy (5.2.3), while using the single particle manipulation technique. This is needed to create interstitials and vacancies and observe how they anneal.

### 5.2.7 E-field effects

The ability to apply an electric field across the cell parallel to the optical axis is desirable. Both dc and low frequency (up to 2 Hz.) ac electric fields of up to 150 volts across the cell depth is preferable. The samples must be isolated from the electrodes to establish the static electric fields. All the measurements listed in sections 5.2.2, 5.2.3, 5.2.4, and 5.2.5 shall be individually possible while the electric field is being applied. This is needed to switch and study the optical properties of many samples.

### 5.2.8 Photonic bandgap studies

The measurement of the unscattered light intensity ( $I$ ) that results from having collimated monochromatic light input over a  $5^\circ \leq \theta < 35^\circ$  incidence angle, with a  $0.25^\circ$  degree resolution, is required. 16384:1 (14-bits) of dynamic range is required for these measurements; the intensity measurement shall have an accuracy of  $\leq 0.1\%$  of full dynamic range. The incident monochromatic light shall cover a range of wavelengths (450nm to 700nm) and shall have a bandwidth no greater than 5nm. Additionally, the incident monochromatic light shall have an adjustable power level and be collimated at the sample, having a diffraction limited spot size that is adjustable in diameter from  $50 - 150\text{ }\mu\text{m}$ . The absolute beam incident power shall be measured to an accuracy and precision of  $\leq 1$  percent. The relative beam stability shall be  $0.1\%$  and the incident beam polarization shall be linear and  $\geq 500:1$ . Optical flare shall be minimized so as to allow measurement of form factors of dilute polystyrene particles down to 5 degrees scattering angle. Temperature stability of  $0.1\text{ }^\circ\text{C}$  is required over the duration of the measurements. High resolution black and white images are required, from 30 Hz to many seconds per image. Recorded images should reflect uniform intensity at the sample (no spatial frequencies higher than  $1/[\text{beam diameter}]$  are allowed and a spatial intensity variation of less than 10% is required). This measurement will be used to quantify the stop-bands of photonic crystals.

### 5.2.9 Apparatus Design Recommendations

Based on our 1-g experience, we see a strong coupling between the science requirements and the engineering apparatus design. Hence, in this section, we describe some apparatus design recommendations that would shed more insight into many of our science requirements.

The apparatus required should be based on an optical microscope. Ideally, it should allow all the science requirements to be achieved. In practice, in these days of faster, better, cheaper, the apparatus should do as much as is feasible given the budgetary constraints. However, all effort must be taken to achieve as many of the required features as possible. This should be done through creative adaptation of the design, within the limited resources available.

It is absolutely feasible to design a microscope that will achieve all the required measurements. An example of such a microscope design is shown in Figure 2. It is based on a design by P. Kaplan and D. Weitz from UPenn (now at Unilever, and Harvard) and results from their experience with all of the microscopic techniques envisioned.

An additional list explaining the details of Figure 2 follows. Note that much of this has been prepared in consultation with Peter Kaplan, a former post doc at Penn who developed the original scattering microscope.

**5.2.9.1 Trans-illumination port:** Needs dual port adapter for switching from bright field to scattering illumination. Bright field illumination can use either a halogen bulb for a white source, or a laser or bright LED if necessary. This should be an incoherent source to avoid speckles in imaging. This is part of Köhler illumination. The laser for scattering is focused on the condenser aperture, to get a collimated beam at the sample. The switching can be done with a two position slider which can be automated. Only one adjustment is required of these optics; the angle of the laser illumination must be changeable. This could be done with a fiber and translation stage. The field diaphragm should also be automated.

**5.2.9.2 Condenser:** Condenser must be automated. Some of this has already been done by Leica, depending on the model. Automation needed includes, switching a polarizer in and out, and rotating it; focussing the condenser; rotating the ring that holds the phase plates, DIC prisms, and a clear aperture for scattering; adjusting the condenser aperture to change the NA of the condenser or eliminate flare for scattering; and possibly rotating in new condensers (this can not be done with current Leica turrets, but can be done with one Zeiss turret). The DIC shear should be adjusted by rotating a half wave plate rather than translating a Wallaston prism.

**5.2.9.3 Epi-illumination Port:** Make into a dual port for fluorescence illumination and for tweezers/confocal. Use laser illumination for the fluorescence excitation. Tweezers should consist of two gimbals mounted conjugate to the back focal plane of the objective. The laser for the tweezers is a plane wave on the gimbaled mirrors. There should also be a dichroic between the laser and the gimbaled mirrors that takes off a portion of the backscattered light, which can then be imaged through a spatial filter onto a PMT for the confocal detection. We may want to consider using dial illumination for the tweezers to allow a YAG type laser for tweezing and a green laser for confocal. These could both illuminate the gimbaled mirrors.

**5.2.9.4 Fluorescence Turret:** This should have four positions: Two are fluorescence filter cubes for different fluorescence dyes, one is a mirror for the tweezers and confocal and the final is a blank for all other microscopy and for the scattering.

**5.2.9.5 Objectives and Prisms:** The objectives will need to be selected based on the requirements of the experiments. This turret is probably already automated. Focussing is done by moving this turret, which also must be automated.

**5.2.9.6 Camera Port:** Used for static light scattering. A good quality, high dynamic range CCD camera, and optics to make a beam block.

**5.2.9.7 Camera Port:** Video detection. Need camera that can be used for bright field, DIC and fluorescence. It probably does not need to be intensified for the fluorescence as most of the fluorescence will be quite intense, as colloidal particles will be used.

**5.2.9.8 Dynamic Scattering:** Single mode fiber mounted on a automated translation stage. At telescope images the back focal plane of the objective onto the plane of the fiber, and the translation allows different scattering wave vectors to be selected.

There are several sliders on the body of the microscope that direct light to different ports and these would have to be automated.

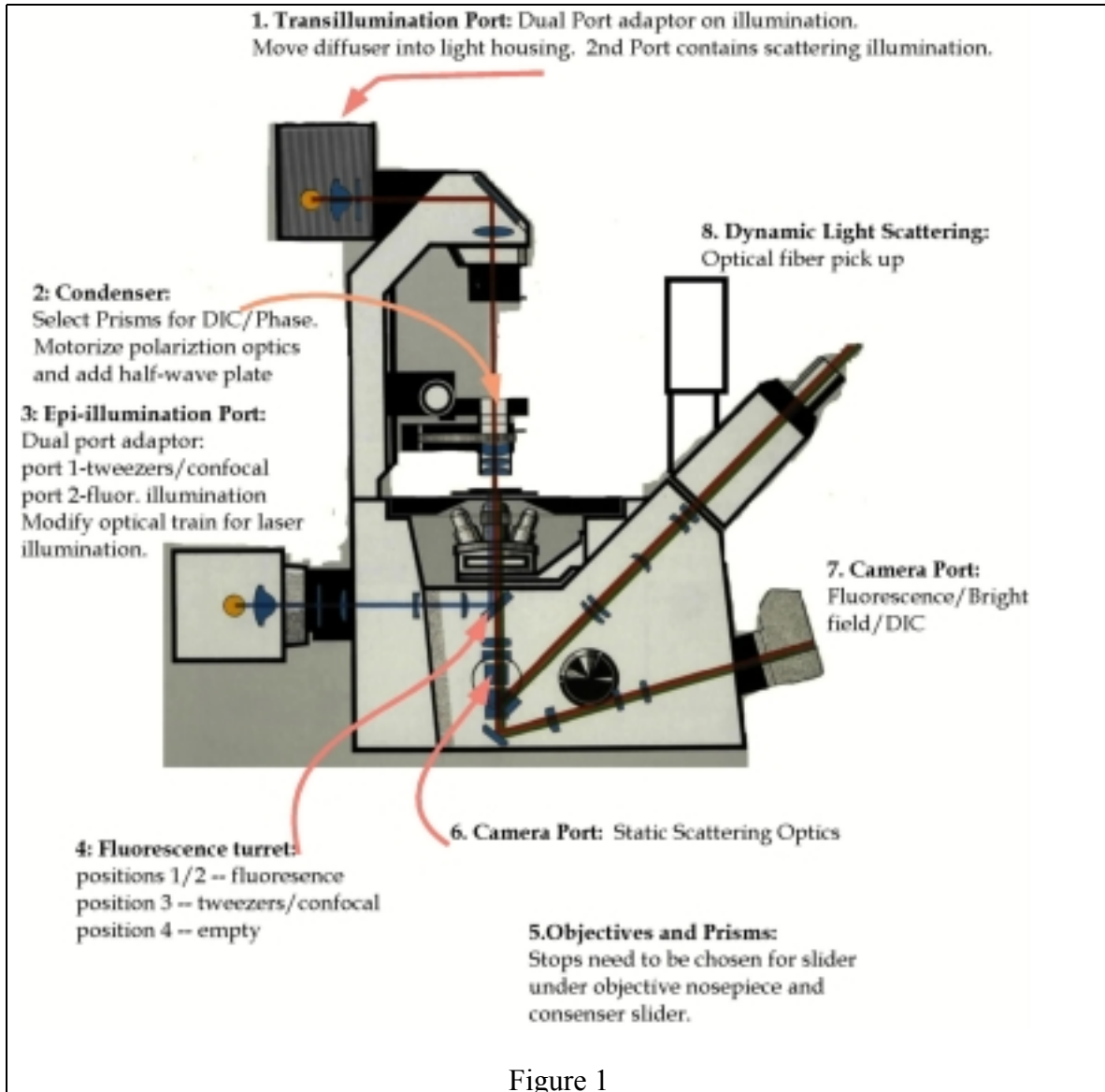


Figure 1

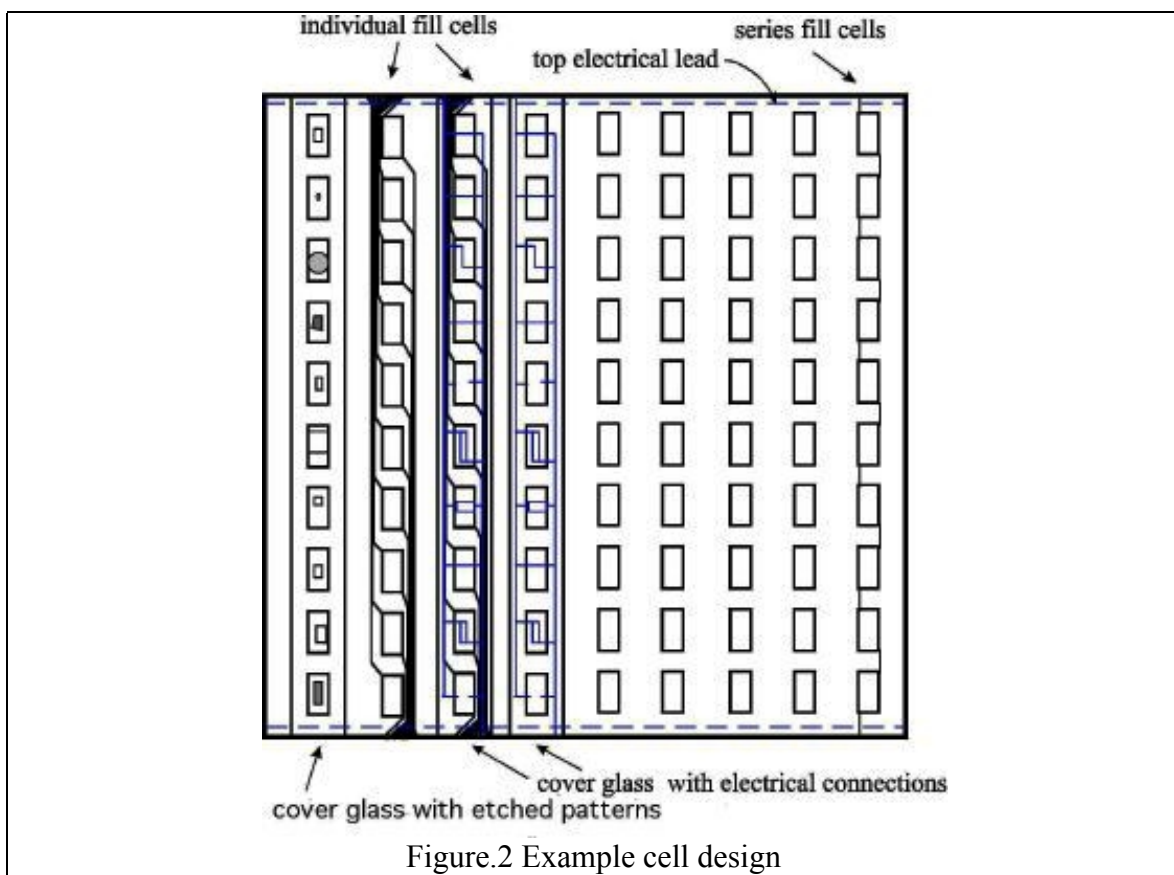
This is not a complete specification of the requirements. However, this provides information about the feasibility of building a microscope that will accomplish all the measurements required. Further details can be delineated after the SCR.

### **5.3 Sample Cell Requirements**

In addition to the sample cell requirements described in section 5.2, the sample cells shall contain the colloidal samples during the length of the experiments, shall provide volumes from 0.1 to 100 micro liters, shall have cell depths from 100 to 200  $\mu\text{m}$ , and shall provide for manipulation and optical viewing of the samples. Around 200 sample cells are needed; this would allow us to measure and study the phase diagram of say, 5 different combinations of materials, each of which we need to grow 3 different classes of crystals, and for each of these around 10 different volume fractions would be of interest. This makes 150 samples. In addition, we want to study a minimum of 50 samples of colloid-polymer mixtures.

#### **5.3.1 Sample Cell Requirements Design Information**

It is essential to have sample cells that can contain enough samples to make the studies proposed here possible. Since the sample volumes required for microscopy are so small, this should not be a problem. A sample size of 1 mm X 1mm X 0.2 mm is adequate for these experiments. Therefore, it should be possible to put a large number of sample cells onto a single holder.



A possible sample cell design is shown in Fig. 2 above. We emphasize that this is only a schematic to illustrate the principle; it has not been drawn to scale. The concept is that the sample cell would be etched onto a piece of glass, roughly the size of a microscope slide, about 25 mm X 100 mm. Each sample would be contained in one of the spherical cells shown schematically. These cells would need to have a diameter of only about 1 to 1.5 mm. Within the cell, a small magnetic wire would be placed; this could be actuated with a small magnet on a motor to stir it to mix the sample. The solid lines are fill tubes, about 100  $\mu\text{m}$  wide. The whole structure would be etched into the glass, about 100  $\mu\text{m}$  to 200  $\mu\text{m}$  deep. The whole sample cell would be covered by a single piece of cover slip glass, defining the upper surface of the cells. Each sample container would be filled through the two fill tubes, shown as the solid lines, using capillary action. Two tubes are shown to allow for the gas to escape through the second as the fluid enters through the first. The tubes could be sealed after the cells are filled. If we assume that the cells are about 1.5 mm wide, they could easily be spaced as close as 2 mm apart. If we take 2.5 mm as a more realistic value, there could still be 40 rows of these on a single slide, providing 240 sample cells. The slides could then be mounted on a translation carousel; a commercial one is available that holds 9 cells the size of each of these. This could potentially provide a total of 2,160 samples. Since at most half of these will be used by PCS-II, there would still be ample number of cells to do the sort of experiments required. This design would have the advantage of allowing different structures to be put on the walls of sample cell, allowing, for example, electrical contact to be made to transparent electrodes on the inner surfaces of the cell.



An alternate design would be to use commercially available rectangular capillary cell that are manufactured in different sizes of rectangles. For example, we could use the capillary cells that are about 150  $\mu$ m depth, and are about 2 mm in width. These could be cut into short length of about 2 mm, filled with the sample, sealed with epoxy and glued to a thicker piece of glass for support. On a single slide it should again be possible to pack about 40 rows of 5 each, or about 200 samples. This would give a total of about 1800 samples in the full holder. This has the advantage of simplicity, but does not allow the sample cell walls to be modified, and does not provide a simple means for applying an electric field.

For some of the experiments, it may be important to use somewhat larger sized sample cells. For example, these could be about 5 mm in diameter, and closer to 1 mm in thickness. These would obviously reduce the total number of sample cells for the same total area of samples. In addition, these would provide more limited optical access, as the higher magnification lenses would not be used. However, in some instances for the colloid-polymer mixtures, the structures of interest may be larger, dictating the use of larger sample cells. We would still be able to use the low magnification lenses and all of the scattering optics; since the structures of interest in these cases would be considerably larger, this would be quite suitable.

We note that the number of sample cells suggested here is only a rough estimate that illustrates the approximate number of cells that can be fit onto a single slide with these concepts. The exact number will depend on the details of the design, and does not have to be the same as these estimates. However, the experiment does require a rather large number of cells. The PCS-II samples will occupy only about half of the sample cells, with the other half being occupied by PH<sup>A</sup>SE samples. The requirement for PCS-II is quite large, primarily because of the need to measure the phase diagrams of some of the binary alloy colloids to determine where the optimum crystallization point is. While this is possible on earth with PMMA particles, it is unlikely to be possible with particles with different densities. The behavior of the PMMA particles will serve as a crucial guideline in determining the properties of the other alloy materials; however it will nevertheless be essential to test these in microgravity, requiring many samples. The size ratio of the particles, their relative concentrations, and the total volume fractions all play important roles. Thus, for example, in ground based tests, a single size ratio is chosen, typically about 5 different relative volume fractions are chosen, and then each is prepared at about 5 different the relative volume fractions of each are prepared. This requires at least 25 samples. In addition, the size ratio should also be tested; if three values were tested, this would require a total of about 75 cells. Allowing for different materials to be studied, the large number of cells would be rapidly filled.

#### **5.4 Delivery Requirements**

Because this proposal is part of an active and ongoing ground-based research program, it is essential not to “freeze” the samples into place any earlier than absolutely necessary. This will allow the very optimum samples to be prepared at the time of the flight. This will ensure that the very best science questions can be addressed. Moreover,

it will ensure that the science remains fresh, interesting and important when the flight is actually flown. This is absolutely essential for this research program.

Therefore sample cell design in the way it is being conducted for PCS-I is unacceptable. In the case of PCS-I, the apparatus is being built around the samples. As a result, the samples are required by the engineering team at least 2 years before the scheduled flight. This would prevent any new science learned over the course of the next two years to impact PCS-I. Given the historical rate of learning new things, this is the wrong approach. Thus for PCS-II, arrangements should be made for very late delivery of the samples. Unlike the PCS-I apparatus, much less alignment will be required.

## **5.5 Atmosphere Requirements**

Normal pressures and temperatures of the cabin environment should suffice for the samples. Because of the stabilizing polymer grafted onto the PMMA spheres, we have to determine the suitable range of temperatures over which the grafting remains stable. This is usually not a problem in the laboratory because temperature extremes are not usually encountered or can be avoided. For the pure solvents the temperature should remain above freezing ( $> -40^{\circ}\text{C}$ ) and below boiling ( $< 190^{\circ}\text{C}$ ) and such that volume changes do not damage the cells.

## **5.6 Vibration Control and Measurement**

For the instrument as a whole, the dc component of gravity is most important for this work. An experiment must be long in duration, but needs no better than  $10^{-3}$  g; averaged over an hour.

However, the samples must not be jarred after homogenization and prior to the light scattering measurements. If a crystallized sample is disturbed, its opalescence will disappear. Accelerations greater than  $10^{-3}$  could disrupt the ordered domains. This experiment is really more sensitive to the lower frequency accelerations. The limit on acceptable average acceleration is given by:  $g_{ave}=10^{-3} (1/t)^{1/2}$ , where  $g_{ave}$  is the allowable average acceleration, and  $t$  is the time frame of interest, expressed in units of hours. Therefore, over a one hour time frame the allowable average acceleration measured at the sample cell is 1 mg (milli-g). Since the vibration environment cannot be controlled, measurement of the vibrational environment during the mission should provide enough information to determine if samples were disturbed during critical periods.

## **5.7 Imaging Requirements**

Downlinked color ccd images of the samples are needed just before and after homogenization. Color images are also required at various stages of the experiments. This will enable the PIs to examine the state of the samples to assess whether equilibration has occurred.

## **5.8 Astronaut Involvement**

Minimal astronaut involvement is envisioned, although the experiment apparatus should have a manual control interface to allow modifications to the experiment procedure in near real time should any problems arise.

## **5.9 Data Requirements**

On-board data storage requirements:

- All visual images, light scattering, and other such data should be time-tagged to MET, and GMT.
- Accelerations in excess of  $10^{-3}$  g should be recorded and time-tagged for comparison with data from the experiment.
- All images and correlograms should be stored with a record of the experimental conditions such as, when the measurement was made, length of measurement, beam and detector positions, wavelength of source, temperature, and laser power for each measurement.
- Temperature is to be recorded with each correlogram and any changes in temperature during quiescent periods should be recorded whenever the temperature changes by more than  $0.1^{\circ}\text{C}$ .
- Visual images of samples are desired just before and after homogenization (5.2.1) and periodically.
- Need capability to periodically downlink any of the above data.

## 5.10 Science Requirements Summary Table

| Parameter  | Section  | Requirement   |
|--|----------|---|
| 5.10.1 Sample Description  | 5.1, 4.1 |   |
| <ul style="list-style-type: none"> <li>Samples (compositions)</li> </ul> |          | <ul style="list-style-type: none"> <li>Binary mixtures of two different sizes of PHSA coated PMMA spheres in an index matching mixture of decalin and tetralin.</li> <li>Binary mixtures of PHSA coated PMMA spheres and other metallic spheres in a mixture of decalin and tetralin.</li> <li>Colloid-polymer (PMMA-polystyrene) samples.</li> <li>Particle sizes: diameters between 10 nm and 5 <math>\mu\text{m}</math></li> <li>Index of refraction: Varies between 1.33 and 1.6. Some samples will be absorbing, having an imaginary component to the index of refraction. Some samples will be metallic, having a negative real part of the dielectric function. Many samples will not be index matched; confocal microscopy will be required to image them.</li> <li>Volume fractions: Between 0.001 and 0.74</li> </ul> |
| 5.10.2 Homogenization  | 5.2.1    | <ul style="list-style-type: none"> <li>be able to homogenize samples one at a time.</li> <li>Simultaneous homogenization and video microscopy to view the sample</li> </ul>   |

|  |                        |   |
|--|------------------------|---|
| <p>5.10.3 Optical Imaging</p> <ul style="list-style-type: none"> <li>Visual Camera Images</li> </ul> | <p>5.2.2<br/>4.2.2</p> | <ul style="list-style-type: none"> <li>High magnification, high resolution color visual images of both highly index matched (to 0.001) and fluorescent colloidal particles (nominally 0.01-5.0<math>\mu</math>m-sized).</li> <li>field of view ranging from 100<math>\mu</math>m x 100<math>\mu</math>m up to the width of the sample cells.</li> <li>dynamic range of at least 256:1 (8-bits).</li> <li>particle centroid resolution of 5nm in all three directions.</li> <li>resolution depth up to 75 <math>\mu</math>m into a sample of 0.1 optical density.</li> <li>record videos at: 30 Hz</li> <li>Capability for some near real time downlink of video and still images to assist with alignment, and homogenization (5.2.1, 5.6)</li> <li>Note that the capabilities that would be needed for imaging the above sample types are: bright field imaging using white light illumination, dark field imaging to view crystal morphology from Bragg scattering, DIC and Phase Contrast to view index matched samples, and fluorescence imaging using filter cubes, and an intensified camera (since the laser used would eventually bleach the dye).</li> </ul> |
|--|------------------------|---|

|  |                              |   |
|--|------------------------------|---|
| 5.10.4 Confocal Microscopy   | 5.2.3                        | <ul style="list-style-type: none"> <li>• High magnification, high contrast three-dimensional visual imaging of highly index matched, highly non-index matched, and fluorescent colloid sample particles.</li> <li>• particles sizes are nominally 0.01-5.0<math>\mu</math>m.</li> <li>• field of view ranging from 100<math>\mu</math>m x 100<math>\mu</math>m to up to the width of the sample cells.</li> <li>• dynamic range of at least 256:1 (8-bits).</li> <li>• particle centroid resolution of 5nm in all three directions.</li> <li>• Resolution depth of up to 75 <math>\mu</math>m into a sample of 0.1 optical density.</li> <li>• high resolution images required at 30 Hz frame rates.</li> </ul> |
| <ul style="list-style-type: none"> <li>• Laser excitation</li> </ul> |                              | <ul style="list-style-type: none"> <li>• Rhodamine dyed PMMA spheres need to be fluoresced. 532 nm laser is known to work well. Note that an intensified camera would be required since the laser used would eventually bleach the dye; adjustable gain, and ability to average signal on camera would be helpful.</li> <li>• Note that an arc lamp can be used for fluorescence excitation; one can also use laser source; it is required that the speckle does not obscure image.</li> </ul>  |
| 5.10.5 <i>Dynamic Light Scattering</i>                               | 5.2.4<br>5.2.9.8<br>5.11.0.6 |   |
| Scattering Angles  |                              | <ul style="list-style-type: none"> <li>• Between 5 and 175 degrees. This could be achieved by using oil or water coupled objective and condenser lenses and varying the angle of the input beam.</li> <li>• Of 0.25 degree resolution</li> </ul>  |

|   |                   |  |
|---|-------------------|--|
| DLS Laser beam illumination and quality | 5.2.4<br>5.11.0.6 | <ul style="list-style-type: none"> <li>• 532nm, or diode laser between 800 and 650 nm. (with same laser source as used for static and Bragg scattering)</li> <li>• 1-30 mW at sample</li> <li>• stability better than 0.1%, beam polarization linear and <math>\geq 500:1</math></li> <li>• adjustable power level</li> <li>• collimated at sample, with diffraction limited spot</li> <li>• spot size adjustable from 5 <math>\mu\text{m}</math> to 600 <math>\mu\text{m}</math> diameter</li> <li>• measure beam incident power levels to an accuracy and precision of <math>\leq 1</math> percent.</li> </ul> |
| DLS signals and Correlations            |                   | <p>Single mode fiber with no lens is recommended for detection optics.</p> <p>at the detector, the signal should be split and fed into two detectors which are cross-correlated to essentially eliminate after-pulsing.</p> <p>Autocorrelation of either detector photon counts or electric current is required, over delay times from 25 nanoseconds to 10000 seconds.</p>  |
| <i>5.10.6 Static Light Scattering</i>   | 5.2.5             |  |
| Scattering Angles                       |                   | <ul style="list-style-type: none"> <li>• Between 5 and 175 degrees. This could be achieved by using oil or water coupled objective and condenser lenses and varying the angle of the input beam.</li> <li>• Of 0.25 degree resolution</li> </ul>   |

|   |       |   |
|---|-------|---|
| SLS Laser beam illumination and quality                                 | 5.2.5 | <ul style="list-style-type: none"> <li>• 532nm, or diode laser between 800 and 650 nm</li> <li>• 0.001 to 30 mW at sample (1 to 30?)</li> <li>• of relative beam stability better than 0.1%, and incident beam polarization linear and <math>\geq 500:1</math>.</li> <li>• adjustable power level</li> <li>• collimated at sample; diffraction limited spot</li> <li>• spot size adjustable from 5 <math>\mu\text{m}</math> to 600 <math>\mu\text{m}</math> diameter</li> <li>• measure beam incident power levels to an accuracy and precision of <math>\leq 1</math> percent.</li> <li>• Optical flare shall be minimized so as to allow measurement of form factors of dilute polystyrene particles down to 5 degrees scattering angle.</li> </ul> |
| Static and Bragg measurements   |       | <ul style="list-style-type: none"> <li>• dynamic range of at least 4096:1 (12-bits).</li> <li>• intensity measurement accuracy of <math>\leq 0.1\%</math> of full dynamic range. Note that adjustable gain, and ability to average signal on camera would be helpful.</li> <li>• High resolution black and white images are required at frame rates of up to 30 Hz over a period of up to 30 seconds per sample (with sequential images taken using log-spaced time increments after the first 30 seconds of 30 Hz images).</li> </ul>  |
| <ul style="list-style-type: none"> <li>• Illuminated volumes</li> </ul> |       | <ul style="list-style-type: none"> <li>- Beam diameter from 5 <math>\mu\text{m}</math> to 100 <math>\mu\text{m}</math> (if already defined, delete from here)</li> </ul>  |



|                                |       |   |
|--------------------------------|-------|---|
| 5.10.7 Laser Tweezers          | 5.2.6 |   |
| Range of scan, force, etc.     |       | <ul style="list-style-type: none"> <li>• Perform single particle manipulation of either a bulk colloidal sample particle, or a particle of a much higher refractive index contrast.</li> <li>• Sufficient power to tweeze off-index particle in PMMA solvent, <math>\Delta n \sim 0.2</math> with 50 pN force</li> <li>• displace particles out of its equilibrium position by up to 20 <math>\mu\text{m}</math></li> <li>• Should be able to tweeze at least 25<math>\mu\text{m}</math> from wall.</li> <li>• Adjustable power control.</li> <li>• Visualization of the directed beam required.</li> <li>• Perform high magnification imaging (5.2.2) or confocal microscopy (5.2.3), while using the single particle manipulation technique.</li> </ul> <p>Laser diode with wavelength between 1100 and 650 nm, or 532 nm can be used. Note: Mara Prentiss at Harvard has assembled simple, inexpensive, flexible laser tweezers that are suitable.</p> <ul style="list-style-type: none"> <li>- Set position control to within 1nm, computer controllable;</li> <li>- point to point scan speed in 1 msec</li> </ul> |
| 5.10.8 Electric Fields Effects | 5.2.7 | <ul style="list-style-type: none"> <li>• Apply E-field parallel to the optical axis <ul style="list-style-type: none"> <li>- Both dc and low frequency (up to 2 Hz.) ac) electric fields of up to 150 volts across the cell depth is desired. As an alternative, it is required, to be able to control e-grids on a single surface such that E-fields can be varied across the cell.</li> </ul> </li> <li>• adjustable accurate to +/- 1 V</li> <li>• electrodes should be isolated from the fluid. (e.g., SiO<sub>2</sub> insulation coated TIO electrodes)</li> <li>• carry out 5.2.3, 5.2.4, 5.2.5, and 5.2.6 (PCS2) measurements simultaneously as the electric fields are applied.</li> </ul>  |

|                                  |            |  |
|----------------------------------|------------|--|
| 5.10.9 Photonic bandgap studies  | 5.4, 5.2.8 | <ul style="list-style-type: none"> <li>• Measure unscattered light intensity from <math>5^{\circ} \leq \theta &lt; 35^{\circ}</math></li> <li>• <math>\leq 0.25</math> degrees of angular resolution</li> <li>• dynamic range of greater than 10000:1 (16384:1(14 bits)) for the intensity measurements, and an accuracy of <math>\leq 0.1\%</math> of full dynamic range.</li> <li>• incident monochromatic light wavelengths range of 450nm to 700nm of bandwidth no greater than 5nm.</li> <li>• The relative beam stability shall be 0.1% and the incident beam polarization shall be linear and <math>\geq 500:1</math>.</li> <li>• adjustable power level for the incident beam,</li> <li>• measure the absolute beam incident power to an accuracy and precision of <math>\leq 1</math> percent.</li> <li>• collimated at sample; diffraction limited spot</li> <li>• spot size adjustable from 50 <math>\mu\text{m}</math> to 150 <math>\mu\text{m}</math> diameter</li> <li>• Optical flare shall be minimized so as to allow measurement of form factors of dilute polystyrene particles down to 5 degrees scattering angle.</li> <li>• High resolution black and white images are required, from 30 Hz to many seconds per image. (1 per minute?) at log spaced time intervals?</li> <li>• Recorded images should reflect uniform beam intensity at the sample such that there are no spatial frequencies higher than <math>1/\text{beam dia.}</math>, and the spatial intensity variation is <math>&lt; 10\%</math></li> </ul> |
| 5.10.10 Sample Cell Requirements | 5.3        | <ul style="list-style-type: none"> <li>• provide adequate containment of the colloidal samples during the length of the experiments.</li> <li>• Sample cell volumes from 0.1 to 100 microliter.</li> <li>• Around 200 sample cells are needed.</li> </ul>  |
| 5.10.11 Atmosphere Requirements  | 5.4        | <ul style="list-style-type: none"> <li>• Normal cabin pressures and temperatures environment is sufficient.</li> </ul>   |

|   |     |   |
|---|-----|---|
| 5.10.12 Vibration Control and Measurement | 5.5 | <ul style="list-style-type: none"> <li>• averaged over an hour, needs no better than <math>10^{-3}</math> g of dc g-level.</li> <li>• Especially after homogenization and prior to the light scattering measurements, avoid jarring disturbances.</li> </ul>  |
| 5.10.13 Access to Image Requirements      | 5.6 | <ul style="list-style-type: none"> <li>• Downlinked color ccd images of the samples are needed just before and after homogenization, and at various stages during crystallization.</li> </ul>   |
| 5.10.14 Astronaut Involvement             | 5.7 | <ul style="list-style-type: none"> <li>• minimal -- depending on the extent of hardware automation. □ □</li> </ul> <p>Data (Storage) Requirements □ 5.8</p> <p>□ • All visual images, light scattering, and other such data should be time-tagged to MET.</p> <ul style="list-style-type: none"> <li>• Accelerations in excess of <math>10^{-3}</math> g should be recorded and time-tagged for comparison with data from the experiment.</li> <li>• Static light scattering, images and correlograms should be stored with a record of the experimental conditions such as, when the measurement was made, length of measurement, beam and detector positions, wavelength of source, temperature, and laser power for each measurement.</li> <li>• Temperature is to be recorded with each correlogram and any changes in temperature during quiescent periods should be recorded whenever the temperature changes by more than <math>0.1^{\circ}\text{C}</math>.</li> <li>• Visual images of samples are desired just before and after homogenization (5.2.1) and periodically.</li> <li>• Need capability to periodically downlink any of the above data.</li> </ul> |

|  |       |   |
|--|-------|---|
| 5.10.15 Apparatus Design Recommendations     | 5.2.9 |   |
| <b>Objective lenses</b>                      |       | <ul style="list-style-type: none"> <li>Chosen to allow range of field of views, from about 100 <math>\mu</math>m to several mm</li> <li>Recommended choice: 5x, 20x, 40x, 100x (and TBD)</li> <li>One lens should be 100x with an NA of at least 1.3 (prefer 1.4); required for tweezers</li> <li>Consider additional water coupled lens</li> <li>Must have appropriate condensers and DIC prisms.</li> </ul> <p>NOTE: Choice of lenses should be done to optimize all requirements, and will depend highly on manufacturer of the microscope.</p> <ul style="list-style-type: none"> <li>White light source for imaging (4.0.1, 4.0.2, Figure 2) Imaging of colloidal particles using Köhler illumination for highest resolution.</li> <li>Also require collimated white light source to look for stop bands in gratings (also required for A. Yodh). This can be done by modifying the focussing optics that image light source onto condenser</li> <li>May also consider monochromatic source if necessary.</li> </ul> |
| <b>Regarding confocal laser</b>              |       | and an intensified camera (since the laser used would eventually bleach the dye).   |
| <b>Regarding confocal Configuration</b>      |       | <p>Either: Pin hole detector after descanning with laser tweezers</p> <ul style="list-style-type: none"> <li>Or: Nipkow disc to allow for real time imaging. Attached to 100x lens.</li> </ul>  |
| <b>Regarding confocal Speed</b>              |       | <ul style="list-style-type: none"> <li>Determined by either tweezers scan rate or Nipkow Disc. Should store data to disk at highest rate possible.</li> </ul>   |
| <b>Scan Range</b>                            |       | Full field of view of highest magnification lens  |
| <b>confocal camera</b>                       |       | <p>Adjustable gain</p> <p>Ability to average signal on camera (these info. are now under laser excitation).</p>   |
| <b>Regarding Types of lenses (condenser)</b> |       | <p>Chosen to complement objectives</p> <ul style="list-style-type: none"> <li>One must be oil or water coupled to allow scattering measurements (avoid total internal reflection that prevents light from escaping sample). (Is under 5 to 175 ... &amp; oil condenser)</li> </ul>  |

|                                    |  |  |
|------------------------------------|--|--|
| <b>regarding correlator boards</b> |  | (Allow for both Brookhaven and ALV computation of the correlation functions (e.g. - Flexible Instruments correlator)) <ul style="list-style-type: none"> <li>• spatial and temporal video images shall be cross-correlated saving a narrow horizontal band 8 pixels high across the middle of the video images (This requirement would be picked up in PHaSE)</li> </ul> |
| <b>regarding Laser tweezers</b>    |  | <ul style="list-style-type: none"> <li>• Field of view of highest magnification lens</li> <li>• Avoids edge effects</li> <li>• be able to turn on and off</li> </ul>   |

### 5.11 Postflight Data Deliverables.

1. Copies of all scripts run.
2. All CCD sample pictures with timestamps.
3. All static scattering data with timestamps.
4. All dynamic light scattering data with timestamps.
5. All rheology data with timestamps (3 possible forms): (needs TBD-rewrites specific to pcs2 experiments)
  - a. Laser tweezers (nonlinear rheology).
  - b. Dynamic light scattering with large particles of a different index of refraction inside the sample of index matched particles.
  - c. Track particles with a microscope.
6. Timeline of when lenses optically aligned, tweezers used and position of tweezers, position of particles, tweezers power, etc.
7. History of various setting, such as, illumination source wavelength and power (when used), filter settings for fluorescence cubes (when used).
  - SAM's data (gravitational acceleration monitoring) in a useful format (e.g. - a graphical plot instead of CDs of acceleration data would help us in making use of acceleration information).

### 5.12 Mission Success Criteria for PCS-2

Complete success is the achievement of all of the science requirements. This means that there will be sufficient information to provide a crosscheck of all data and calculated factors.

Processing, manipulation and characterization of the samples in micro-gravity are as important as the measurements during the experiments themselves. e.g., sample homogenization is essential to conduct of any of the flight experiments. This allows for the dissolution of the crystallites that have formed in 1g before launch, and provides a proper starting point in zero g.

| <b>% Success</b>  | <b>Accomplishment</b>  |
|-------------------|--|
| greater than 100% | Complete all measurements on all cells, synthesize new materials, uncover unexpected results.  |
| 100%              | Homogenize and complete all measurements on all cells.<br>Use a microscope and visualize the samples -- focus the microscope remotely and take pictures.<br>Measure properties (especially structural measurements) of binary alloy crystals, and of colloid polymer mixtures. |
| 90%               | Homogenize and complete 90% of the measurements on cells with binary alloys and colloid polymer mixtures. Identify any new binary alloy colloidal crystals structures formed, and study them with both microscopy and Bragg scattering.  |
| 75%               | Homogenize and complete 75% of the measurements on cells with binary alloys of different materials, and with colloid polymer mixtures. Complete microscopy or scattering measurements.   |
| 60%               | Partial measurements on some cells. Either microscopy or scattering.   |

## **6 Test Matrix**

The current plan for this experiment is to conduct it over a period of about 20 months of flight. As such, new information will undoubtedly be learned, and the nature of the experiments conducted will evolve to take advantage of this new information. As a result, it is essential to allow the PI's as much control over all the instrument capabilities from the ground as possible, and as much time to perform experiments as possible. The following test matrices should be viewed as representative of the sort of experiments that will be conducted.

## PCS-2 TEST MATRIX . Version 4.2

9/14/00.

| SAMPLE # | SAMPLE TYPE  | DAY #                             | GENERAL DESCRIPTION OF TEST       | MANIPULATION, DIAGNOSTICS, (AND ACQUISITION RATE)  | <i>Test procedure: Sequence. &amp; Ball park Time taken.</i>   | ACQUISITION FREQUENCY  |
|----------|--|-----------------------------------|-----------------------------------|--|--|--|
| 1-30     | <b>Binary Colloids</b><br>~8 Type AB<br>~8 Type AB <sub>2</sub><br>~7 Type AB <sub>6</sub><br>~7 Type AB <sub>13</sub><br><b>PMMA</b> in slightly off index-match solvent, each with a fixed volume fraction. Diameter 0.6 $\mu$ - 0.9 $\mu$ . | 1                                 | Homogenize samples.               | Each sample is individually stirred and observed with 10x lens to assure homogeneous melting. Can stir all one by one and then go to take pictures since the crystallization is very slow. | Stir each sample one by one. [Around one minute each].<br><br>Take pictures (10x and 20x) to evaluate homogeneous mixing. [Around one minute for each picture].<br><br>Using software, characterize the sample homogeneity after mixing. [Around one minute for each picture].<br><br>Total time: 2 Hrs. | once.  |
|          |  | 2 ~ 90 (or until crystals appear) | Begin growth studies of crystals. | (Once monthly, until crystals appear,) image each sample using either bright field or DIC microscopy to identify nucleation of crystals.   | Using either bright field or DIC microscopy, (depending upon the particle-solvent index mismatch), identify nucleation of crystals. [Automate these procedures to do in ~ 5 minutes per sample; time for 30 samples $\approx$ 150 minutes = 2.5 hrs.]<br><br>Total time: 900 mins = 15 hours.            | once monthly, and after 60 days, once every week. Thus, ~ 6 times. |



|  |  |       |   |   |   |            |
|--|--|-------|---|---|---|------------|
|  |  | 90-99 | <p>Continue growth studies of crystals.</p> <p>Study selected samples/crystals, and determine crystal structures.</p> | <p>Image samples that show crystals using DIC and bright field microscopy,</p> <p>record selected samples in video at various magnifications.</p> | <p>Image selected samples (around 18) that show crystals using either bright field or DIC microscopy.</p> <p>Record (video) selected (around 18) samples with x5, x20, and x100 objectives for 2 minutes each.<br/>[An average of 10 minutes per sample for brightfield, DIC, and video. Hence, <math>\sim 18 \times 10 = 180</math> minutes. =3 hrs.]</p> <p>Study selected samples/crystals (around 12) using confocal microscopy to determine the crystal structure, (defects, orientations, etc.)<br/>[Time taken for confocal microscopy and analysis depends on the polydispersity (here, A, B sizes) of the sample. For these samples, it can typically take 10 minutes each; Hence, <math>\sim 12 \times 10 = 120</math> mins = 2 hrs.]</p> <p>Total time: 50 hrs</p> | Every Day. |
|--|--|-------|---|---|---|------------|

|       |                                     |      |  |  |  |  |
|-------|-------------------------------------|------|--|--|--|--|
|       |                                     | > 99 | <p>Continue growth studies of crystals.</p> <p>Determine crystal structure and lattice defects.</p> <p>Locate grain boundaries;</p> <p>use laser tweezers to manipulate crystal lattice defects, and record responses.</p> | <p>Use high magnification confocal imaging.</p> <p>Use objective (using say, DIC) - to locate grain boundary.</p> <p>Use laser tweezers to manipulate crystal lattice defects; simultaneously, do high magnification video imaging or confocal microscopy.</p> | <p>High magnification confocal imaging for several minutes. Select and study around 18 crystals at around 10 minutes each. [18 x 10 = 180 mins = 3 hrs.]</p> <p>Locate grain boundaries of selected crystals of interest (around 6), [~ 1 hr at 10mins per crystal]</p> <p>and, use laser tweezers to manipulate crystal lattice defects, and record the activity using high magnification video, or confocal data. [~ 1 hr at 10mins per crystal.]</p> <p>Total time: 5 hrs x 4 =20 hrs.<br/>TOTAL time for samples1-30 = 87 hrs.</p> | <p>once every three weeks, (say, on days 99, 120,140, and160).</p> |
| 31-60 | <b>PMMA-Silica</b><br>Binary Alloys |      | Nucleation, growth, and morphology of crystals.  | Same as <b>PMMA</b>  | TOTAL time for samples 31-60 = 87 hrs.   | Same as <b>PMMA</b>  |

|       |   |                                  |  |   |   |  |
|-------|---|----------------------------------|--|---|---|--|
| 61-90 | <b>PMMA-Metal Colloids</b><br>Binary Alloys | Same as <b>PMM A</b> , plus >120 | <p>Nucleation, growth, and morphology of crystals.</p> <p>Study the structure, its evolution, and defects.</p> | <p>Same as <b>PMMA</b>, plus</p> <p>Study details of crystal structures using confocal microscopy.</p> <p><i>Measure stop bands.</i> (spectrophotometry:)</p> | <p>Total time for samples 61-90 until 120 days = 77 hrs.</p> <p>High magnification confocal imaging for several minutes. Select and study around 18 crystals at around 10 minutes each. [18 x 10 = 180 mins = 3 hrs.]</p> <p>Spectrophotometry **: If using white incident light, and color CCD: For selected (1 to 4) samples/crystals, vary incident angles (0 to 60 degrees), and for various cylindrical angles (360 degrees), test bandgaps at coarse levels first, and then at a fine 0.25 degree resolution level at selected incident angles of interest. [estimated time ~ 30 minutes for each sample/crystal of interest.]</p> <p>If using spectrophotometer with a range of wavelengths, and color CCD camera: [the estimated time for the above procedure, at 2 hrs for each sample/crystal of interest, is 8 hrs.] TOTAL time for samples 61-90: 77 hrs + ((3+8)hrs x 2) = 99 hrs.</p> | <p>then, once every three weeks. (say, on days 140, and 160)</p> |
|-------|---|----------------------------------|--|---|---|--|

|        |  |   |  |   |  |  |
|--------|--|---|--|---|--|--|
| 91-120 | <b>PMMA-Liquid<br/>Crystal<br/>Binary Alloys</b> | Same<br>as<br><b>PMM<br/>A,</b><br>plus<br>>120 | Nucleation,<br>growth,<br>and<br>morpholog<br>y of<br>crystals.<br><br>Study the<br>structure,<br>its<br>evolution,<br>and<br>defects. | Same as <b>PMMA,</b><br>plus<br><br>Study details of crystal<br>structures using<br>confocal microscopy.<br><br><i>Measure stop bands.</i><br>(spectrophotometer)<br><br>Apply E-fields and<br>study the effect on<br>crystals. | Total time for samples 91-120 until<br>120 days = 77 hrs.<br><br>High magnification confocal imaging<br>for several minutes. Select and study<br>around 18 crystals at around 10<br>minutes each. [18 x 10 = 180 mins = 3<br>hrs.]<br><br>See **<br>One to 4 crystals would be analyzed:<br>[Estimated time: 8 hrs]<br><br>Select one or two crystals,<br>Apply DC (~12 volts) electric fields in<br>the available configuration(s),<br>and study by polarization microscopy,<br>and spectrophotometer and use<br>Confocal microscopy on selected<br>samples, while the E-field is applied.<br>[~ 1 hr]<br><br>TOTAL time for samples 91-120:<br>77hrs + ((3+8+1)hrs x 2) = 101 hrs. | then, once<br>every three<br>weeks (say,<br>on days140,<br>and160) |
|--------|--|---|--|---|--|--|

|         |   |  |   |  |   |   |
|---------|---|--|---|--|---|---|
| 121-150 | <b>PMMA-Semi-conductor</b><br>Binary Alloys   | Same as <b>PMM A</b> , plus >120 ...<br><br>(Thus, same as PMMA-Metal colloid) | Nucleation, growth, and morphology of crystals.<br><br>Study the structure, its evolution, and defects. | Same as <b>PMMA</b> , plus same as above (samples 91-120), but without E-fields aspects.<br><b>i.e.:</b><br><br>Study details of crystal structures using confocal microscopy.<br><br><i>Measure stop bands.</i> (spectrophotometer) | Total time for samples 121-150 until 120 days = 77 hrs.<br><br>High magnification confocal imaging for several minutes. Select and study around 18 crystals at around 10 minutes each. [18 x 10 = 180 mins = 3 hrs.]<br><br>See **<br>One to 4 crystals would be analyzed: [Estimated time: 8 hrs]<br>TOTAL time for samples 121-150: 77 hrs + ((3+8)hrs x 2) = 99 hrs. | then, once every three weeks. (say, on days 140, and 160) |
| 151-180 | <b>Silica-Liquid-crystal</b><br>Binary Alloys | Same as <b>PMM A</b> , plus >120   | Nucleation, growth, and morphology of crystals.   | Same as <b>PMMA</b> , plus same as samples 91-120.   | Same as samples 91-120: i.e.<br>Total time for samples 151-180 until 120 days = 77 hrs.<br><br>High magnification confocal imaging for several minutes. Select and study around 18 crystals at around 10 minutes each. [18 x 10 = 180 mins = 3 hrs.]<br><br>See **<br>One to 4 crystals would be analyzed: [Estimated time: 8 hrs]                                      | then, once every three weeks (say, on days 140, and 160)  |

|         |   |                                  |  |   |  |  |
|---------|---|----------------------------------|--|---|--|--|
|         |   |                                  |  |   | <p>Select one or two crystals,<br/>Apply DC (~12 volts) electric fields in the available configuration(s), and study by polarization microscopy, and spectrophotometer, and use Confocal microscopy on selected samples, while the field is applied.<br/>[~ 1 hr]</p> <p>TOTAL time for samples 151-180:<br/>77 hrs + ((3+8+1)hrs x 2) = 101 hrs.</p>                                |  |
| 181-210 | <b>Silica-Semi-conductor</b><br>Binary Alloys | Same as <b>PMM A</b> , plus >120 | <p>Nucleation, growth, and morphology of crystals.</p> <p>Study the structure, its evolution, and defects.</p> | <p>Same as <b>PMMA</b>, plus same as PMMA-semiconductor samples (121-150).</p> <p>i.e:</p> <p>(Study details of crystal structures using confocal microscopy.</p> <p><i>Measure stop bands.</i> (spectrophotometer)</p> | <p>Total time for samples 181-210 until 120 days = 77 hrs.</p> <p>High magnification confocal imaging for several minutes. Select and study around 18 crystals at around 10 minutes each. [18 x 10 = 180 mins = 3 hrs.]</p> <p>See **<br/>One to 4 crystals would be analyzed: [Estimated time: 8 hrs]<br/>TOTAL time for samples 181-210:<br/>77 hrs + ((3+8)hrs x 2) = 99 hrs.</p> | <p>then, once every three weeks. (say, on days 140, and 160)</p> |

|         |   |   |                     |   |   |      |
|---------|---|---|---------------------|---|---|------|
| 211-240 | <p><b>PMMA Colloid + Polymer GEL</b><br/>Many different size ratios, colloid concentrations and polymer concentrations.</p> <p>Particles in slightly off index-match solvent, each with a fixed volume fraction.<br/>Dia. 0.3 <math>\mu</math> -1.0 <math>\mu</math>.</p> | 1 | Homogenize samples. | Each sample is individually stirred and observed with 10x lens to assure homogeneous melting. | <p>Stir each sample one by one. [Around one minute each].</p> <p>Take pictures (10x and 20x) to evaluate homogeneous mixing. [Around one minute for each picture].</p> <p>Using software, characterize the sample homogeneity after mixing. [Around one minute for each picture].</p> <p>Total time: 2 Hrs.</p> | once |
|---------|---|---|---------------------|---|---|------|

|  |  |  |  |   |  |   |
|--|--|--|--|---|--|---|
|  |  | 1-8<br>AND,<br>on days<br>14, 21,<br>and 28. | Gel<br>Studies:<br>Study<br>structure<br>and its<br>evolution,<br>and<br>strength. | <p>Using confocal microscopy determine the gel structure.</p> <p>Do a long confocal microscopy measurement.</p> | <p>Using either bright field or DIC microscopy, (depending upon the particle-solvent index mismatch), image gel structures of samples.<br/>[Automate these procedures to do in ~ 5 minutes per sample; time for 30 samples = ~ 150 minutes = 2.5 hrs.]</p> <p>Use confocal microscopy to determine the gel structure, and record (video) of selected (around 18) samples with x5, x20, and x100 objectives for 2 minutes each.<br/>[An average of 10 minutes per sample for brightfield, DIC, and video. Hence, ~ 18 x 10 = 180 minutes. = 3 hrs.]</p> <p>Do one one hour long confocal microscopy measurement on a selected sample.</p> <p>Total time: 6.5 x 11 = 71.5 hrs.</p> | 1-8 Every day(7 days)<br>AND, once weekly thereafter until day 28. (days 14, 21, 28). |
|--|--|--|--|---|--|---|



|  |  |   |  |  |  |   |
|--|--|---|--|--|--|---|
|  |  | thereafter, with around 1, 2, 3, and 4 weeks between returns, if, and only if, crystals appear: | <p>Crystal structures and morphology</p> <p>Determine crystal structure and lattice defects.</p> <p>Locate grain boundaries; use laser tweezers to manipulate crystal lattice defects, and record responses.</p> <p>Determine gel strength</p> | <p>Use high magnification confocal imaging for several minutes.</p> <p>Use objective (using say, DIC) - to locate grain boundary.</p> <p>Use laser tweezers to manipulate crystal lattice defects; simultaneously, do high magnification video imaging or confocal microscopy.</p> | <p>[Time taken: <math>\sim 30 \times 10 = 300</math> mins = 5 hrs.]</p> <p>Locate grain boundaries of selected crystals of interest (around 6), [<math>\sim 1</math> hr at 10mins per crystal]</p> <p>and, use laser tweezers to manipulate crystal lattice defects, and record the activity using high magnification video, or confocal data.<br/>[<math>\sim 1</math> hr at 10mins per crystal.]</p> <p>Nominally, do one one hour long confocal microscopy measurement on a selected sample. [<math>\sim 1</math> hr]</p> <p>Total time: <math>8 \text{ hrs} \times 4 = 32 \text{ hrs}</math><br/>TOTAL time for samples 211-240:<br/><math>73.5 + 32 \approx 106 \text{ hrs.}</math></p> | <p>If and only if crystals appear.<br/>(36, 50, 71, 100).</p> |
|--|--|---|--|--|--|---|

|         |   |  |  |  |  |   |
|---------|---|--|--|--|--|---|
| 241-270 | <b>PMMA Colloid + Polymer Two Phase Gas-Solid</b> | 1  | Homogenize samples.  | Each sample is individually stirred and observed with 10x lens to assure homogeneous melting.  | <p>Stir each sample one by one. [Around one minute each].</p> <p>Take pictures (10x and 20x) to evaluate homogeneous mixing. [Around one minute for each picture].</p> <p>Using software, characterize the sample homogeneity after mixing. [Around one minute for each picture].</p> <p>Total time: 2 Hrs.</p>  | once.   |
|         |   | 1-7 daily<br>AND<br>>7 weekly thereafter | Crystal growth, morphology, and structure.<br>Gas dynamics<br><br>Study selected samples/crystals, and determine | Image samples that show crystals using DIC and bright field microscopy,<br><br>record selected samples in video at various magnifications.<br><br>Use high magnification confocal imaging for several minutes. | Using either bright field or DIC microscopy, (depending upon the particle-solvent index mismatch), identify nucleation of crystals.<br><br>Record (video) selected (around 12) samples with x5, x20, and x100 objectives for 2 minutes each.<br>[An average of 10 minutes per sample for brightfield, DIC, and video. Hence, $\sim 12 \times 10 = 120$ minutes. =2 hrs.]<br><br>Study selected samples/crystals (around 12) using confocal microscopy to determine the crystal structure, (defects, orientations, etc.)<br>[Time taken for confocal microscopy and | 1-7 daily<br>AND<br>>7 weekly thereafter<br><br>(say, on days 14, 21, 29, 43, 57, 71, 92, 113, 134) = 16 times. |

|  |  |  |   |  |  |  |
|--|--|--|---|--|--|--|
|  |  |  | <p>crystal structures and lattice defects.</p> <p>Determine dynamics of crystal.</p> <p>Locate grain boundaries;</p> <p>use laser tweezers to manipulate crystal lattice defects, and record responses.</p> | <p>Nominally, highest speed confocal microscopy measurements.</p> <p>Use objective (using say, DIC) - to locate grain boundary.</p> <p>Use laser tweezers to manipulate crystal lattice defects; simultaneously, do high magnification video imaging or confocal microscopy.</p> | <p>analysis depends on the polydispersity (here, various gels) of the sample. For these samples, it can typically take 10 minutes each; Hence, <math>\sim 12 \times 10 = 120</math> mins = 2 hrs.]</p> <p>Locate grain boundaries and crystal lattice defects of selected crystals of interest (around 6), [<math>\sim 1</math> hr at 10mins per crystal]</p> <p>and, use laser tweezers to manipulate crystal lattice defects, and record the activity using high magnification video, or confocal microscopy. [<math>\sim 1</math> hr at 10mins per crystal.]</p> <p>Total time:<br/> <math>2 \text{ hrs} + ((2+2+1+1)\text{hrs} \times 16) = 98 \text{ hrs}</math><br/> Thus,<br/> TOTAL time for samples 241-270 = 98 hrs.</p> |  |
|--|--|--|---|--|--|--|

|         |   |                             |  |  |  |   |
|---------|---|-----------------------------|--|--|--|---|
| 271-300 | <b>PMMA Colloid + Polymer</b><br><b>Three Phase</b><br>Gas-Liquid-Solid Samples | 1-6 daily<br>AND >6 weekly. | Crystal growth, morphology, and structure. Gas and liquid droplet dynamics<br><br>Determine shape and time dependent fluctuations in liquid droplets.<br><br>Determine dynamics of particles in liquid droplets. | Same as <b>PMMA Two-Phase, PLUS</b><br><br>Video imaging for several minutes<br><br>Study details of liquid droplets region using confocal microscopy. | Same as <b>PMMA Two-Phase</b> ,<br><br>Locate liquid droplets and perform video imaging for several minutes<br>[Estimated extra time: 1 hrs per session.]<br><br>Study using confocal microscopy<br>[Estimated extra time: 1 hrs per session.]<br><br>Thus, $(6+2) \times 13 = 104$ hrs<br><br>TOTAL time for samples 271-300 = 104 hrs. | 1-7 daily<br><br>AND<br><br>>7 weekly thereafter<br><br>(say, on days 14, 21, 35, 49, 70, 91) = 13 times. |
|         |   |                             |  |  | TOTAL time= 87 +87 + 99 + 101 +99 + 101+99+106+98+104 = =981 hrs.  |   |

## **7 Principal Investigator's Requirements**

### **7.1 Research Equipment**

#### **7.1.1 Preflight**

The design of the experimental apparatus is relatively complicated; it is a sophisticated piece of equipment even when located in a lab. To be flown, it must be totally automated to allow operation without any crew intervention. Once it is aboard the ISS, experiments will be conducted over the course of many months. In order to fully understand its capabilities to ensure that the best science possible is performed, it is essential that the PI's be given ample time to use the apparatus, or an apparatus as close to the flight version as possible. Thus, when the choice of the exact microscope is made, an identical one should be put in the PI's lab. In addition, as the different parts of the microscope are assembled, copies should be supplied to the one in the PI's lab. This should include in particular all the automated control of the microscope and versions of the software control that mimic the flight control software. This is essential to allow full knowledge of the operation of the microscope.

In addition to having continual access to an engineering model in the lab, there should be some time available to test the actual flight apparatus, or a full engineering model. This time can be significantly reduced if a reasonably complete engineering model is supplied as it is constructed, and if this mimics the behavior of the flight model. Nevertheless, some time will be required to learn how the flight apparatus functions.

#### **7.1.2 Postflight**

Access to the flight samples and a functional engineering model of the equipment would allow some of the observations to be tested, and the conditions to be repeated on the ground. This may prove important in interpretation of the data obtained.

### **7.2 Apparatus design assistance**

The proposed apparatus is sufficiently complexity, and the experience of the design team at NASA LeRC with microscopy is sufficiently limited, that some of the design work should be carried out concurrently by the PI's. A good model for the effectiveness of this is the design of the very small angle camera that is being incorporated into the PCS-I apparatus; a post doc, Luca Cipelletti, developed the instrument in parallel with the flight instrument. This has provided essential guidance to the flight instrument development and has ensured that when compromises must be made, the impact on the science is understood. In addition, the availability of a very similar instrument at Penn/Harvard has provided essential experience in its use, that will prove critical to future flight experiments.

A similar arrangement should be done for the case of the PCS-II microscope. All of the desired elements have been set up on microscopes at Penn, and now at Harvard over the last few years. However, they have never been incorporated into a single unit.

An effort to do this, on a version of a microscope as close to the flight one as possible, must be done in the PI's lab concurrently with the effort at NASA LeRC. For example, the specifications shown in the previous section were based on our experience with an inverted Leica microscope, which is available in the lab. There is no problem in principle to do the same with an upright microscope, or with one from a different manufacturer, but this microscope must be available, and the details must be worked out. This should be done concurrently in the PI's lab to take advantage of all the accumulated experience in the use of microscopes for these experiments.

### **7.3 Consultation**

Peter Kaplan is an expert in microscopy, and has designed much of the scattering microscope currently assembled at Harvard. He should be hired as a part-time consultant on microscopy. He is a former post doc at Penn, and is currently employed at Unilever. However, he is able to consult on this project.

### **7.4 Grants and Contracts**

#### **Grants:**

The current resources of the grant are fully expended in the support of PCS-I, and this will not change until well after the flight. Since the time scale is so rushed for design and assembly of the apparatus for PCS-II, support for an additional post doc to work on the apparatus will be critical. This post doc would be based at Harvard where there is considerable expertise in microscopy and would be responsible for the design and assembly of an engineering model of the microscope, based on the flight version. The post doc would help design the details of the optics, and would help resolve the problems that arise. Basing the post doc at Harvard, would ensure that all the existent expertise in microscopy would be harnessed in the design of the flight version. In addition, by being directly responsible for the science, the post doc would ensure that the science requirements are met as the inevitable changes and compromises are made during the design process. Such a post doc is essential if this project is to be successful.

#### **Contracts:**

The work at Edinburgh is support through a sub contract from Harvard. Currently there a post doc, Andy Schofield, makes all the PMMA particles for all the experiments. He also cleans these particles, and uses them to study the phase behavior of the binary alloys. These experiments are critical for PCS-I. The key new sample requirement for PCS-II is the use of additional particles of different materials. This requires a rather large synthesis effort as these particles must be made compatible with each other. While Andy has had some success in this, his available time for this is highly restricted by his commitments for PCS-I. Thus success for PCS-II would be considerably enhanced by having a second post doc to work with Andy at making new particles of different materials, ensuring that they are compatible with the others and studying their phase properties.

## **7.5 Services**

Film Developing:

Software Development:

## **8 Other Requirement**

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